PB84-159904

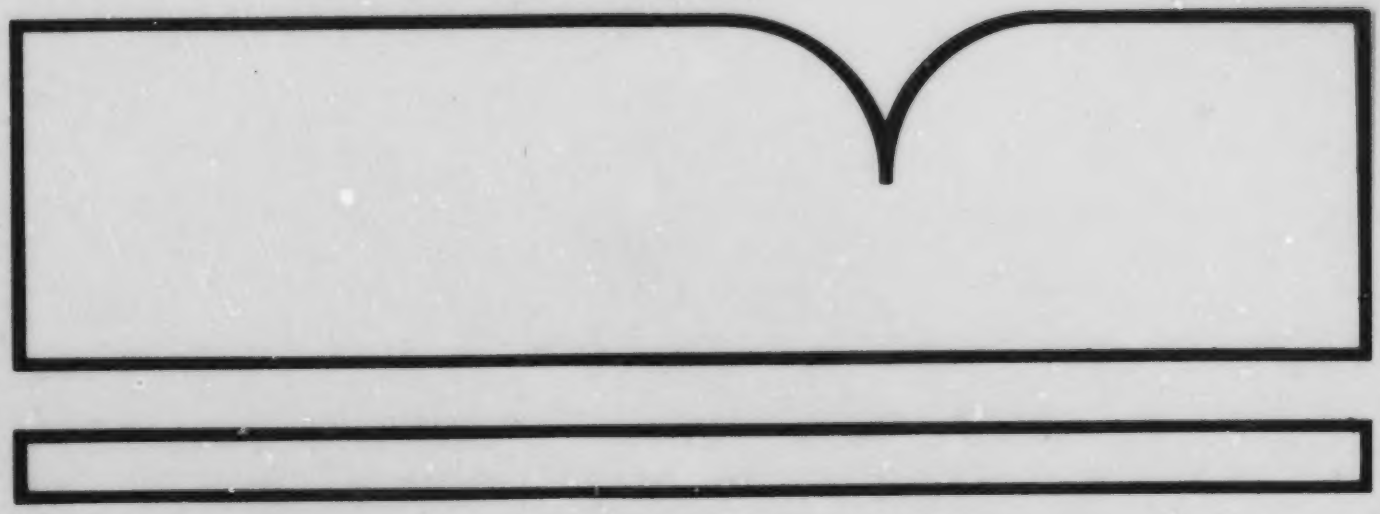
Priority Pollutants in the Cedar Creek Wastewater Reclamation - Recharge Facilities

Nassau County Dept. of Public Works
Wantaugh, NY

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Feb 84



U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-159904

EPA-600/2-84-061
February 1984

PRIORITY POLLUTANTS IN THE CEDAR CREEK WASTEWATER RECLAMATION - RECHARGE FACILITIES

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CINCINNATI, OHIO 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-84-061		PB84 159904

4. TITLE AND SUBTITLE	5. REPORT DATE
Priority Pollutants in the Cedar Creek Wastewater Reclamation - Recharge Facilities	February 1984
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
I. D. Brisbin, S. H. Ahn, R. I. Foster, S. A. Labunski, and J. A. Oliva	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Department of Public Works Nassau County P.O. Box 88 Wantaugh, New York 11793	AZBIB
	11. CONTRACT/GRANT NO.
	CR-804654
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory-Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Final 4-80 to 10-82
	14. SPONSORING AGENCY CODE EPA 600/14

15. SUPPLEMENTARY NOTES
Project Officer: John N. English (513)684-7613

16. ABSTRACT

The Cedar Creek Wastewater Reclamation Plant (CCWRP) located in Nassau County, NY is a 0.24 m^3/s (5.5 mgd) advanced wastewater treatment (AWT) plant designed to produce a high quality effluent suitable for groundwater recharge. The CCWRP was constructed as a demonstration project under a U.S. Environmental Protection Agency (EPA) grant by additions and modifications to the main 1.96 m^3/s (45 mgd) Cedar Creek Water Pollution Control Plant (CCWPCP). Operation of the CCWRP began in April 1980 and groundwater recharge operations began in October 1982. This research project was initiated with the overall objective of providing preliminary data on the presence of priority pollutants in the Cedar Creek Wastewater Reclamation - Recharge Facilities. The results indicate that 72 priority pollutants were identified in the influent and that significant removals (99%) of some individual compounds were achieved by the plant processes. The data also indicate that the concentration of trihalomethanes increases during both the treatment and recharge operations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Water Reclamation, Reuse, Wastewater Treatment, Tertiary Treatment, Potable, Priority Pollutants, Water Treatment, Advanced Wastewater Treatment, Pollutants, Contaminants, Groundwater		13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	92
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

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Although the information described in this article has been funded wholly or in part by the United States Environmental Protection Agency through assistance agreement number R804654-01 to Department of Public Works of Nassau County, New York, it has not been subjected to the Agency's required peer and administrative review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report contains the results of a preliminary priority pollutant removal study to evaluate the performance of an advanced wastewater treatment plant designed to treat municipal wastewater so that it can be used to recharge a groundwater system. Through this project, the feasibility of replenishing groundwater supplies and reclaiming water for future use is being established.

Francis T. Mayo
Director
Municipal Environmental
Research Laboratory

ABSTRACT

The Cedar Creek Wastewater Reclamation Plant (CCWRP) located in Nassau County, NY is a 0.24 m^3/s (5.5 mgd) advanced wastewater treatment (AWT) plant designed to produce a high quality effluent suitable for groundwater recharge. The CCWRP was constructed as a demonstration project under a U. S. Environmental Protection Agency (EPA) grant by additions and modifications to the main 1.96 m^3/s (45 mgd) Cedar Creek Water Pollution Control Plant (CCWPCP). The processes used at the CCWRP are grit removal, chemically aided primary clarification, suspended growth nitrification/denitrification, post aeration, chemically aided sedimentation, dual media filtration, carbon adsorption and chlorine disinfection. Plant operations began in April 1980 and groundwater recharge operations began in October 1982. This report contains the results of a preliminary study designed to indicate the levels of priority pollutants in the influent and process effluents of the CCWRP. This project was not planned to be an extensive evaluation of the plant performance and reliability in meeting effluent criteria.

This study began with the collection of 3 sets of samples from the CCWRP influent and effluent in April, May, and June 1981. The results of these first three sampling events were used as a preliminary measure of overall plant performance, and as additional data for the New York State Department of Environmental Conservation (NYSDEC) to use for finalizing a State Pollution Discharge Elimination System (SPDES) permit for groundwater recharge. In addition to utilizing standard EPA priority pollutant analytical protocols, an XAD resin was used in the first sampling event to concentrate the organics in the effluent. During the three sampling events a total of 72 priority pollutants in trace concentrations were identified in the influent. Thirty-one (31) non-priority trace organics were also identified, but not quantified. Based on total mass of identified compounds, average plant priority pollutant removal efficiencies for the three sampling events were: volatile organics - 85%, extractable organics - 80%, pesticides/PCBs - 47%, and metals - 64%. Results obtained using an XAD resin methodology indicate that greater than 99% removal is obtained for most of the extractables.

A total of 23 samples were collected during the latter part of 1982 to evaluate the effectiveness of individual treatment processes for priority pollutant removals. Based on the total

pollutant mass for 3 samples obtained for determining priority pollutant removals in primary treatment, 41% of the volatile organics mass was removed. Results of the 3 sampling events for evaluating biological process performance indicate that the volatile organic removal increased to >99%. Forty-nine percent of the heavy metals were removed through primary treatment and further biological treatment increased the removal to 92%. For most of the samples, the extractable organics were below the quantification limit; thus, removal efficiencies could not be determined.

Data indicated that chlorination may enhance the formation of priority pollutants. A total of 5 volatile organics were detected in the carbon adsorber effluent during 3 sampling events. After chlorination, a total of 10 volatile organics were detected in the chlorinated effluent. It appears that several volatile organics - most notably, trihalomethanes - were formed in the AWT facilities. These compounds were, in order of decreasing concentration: bromoform, dibromochloromethane, chloroform, and bromodichloromethane.

Baseline concentrations of priority pollutants in the aquifer below the recharge site were determined prior to recharge operations. While not detected in any of the monitoring wells before recharge, preliminary results from 2 of the 6 wells indicate that trihalomethanes were detected at an average concentration of 257 µg/l after recharge and the trihalomethanes appear to increase in concentration in the ground with distance from the recharge point.

This report was submitted in partial fulfillment of cooperative agreement No. CR804654 by the Department of Public Works of Nassau County, New York under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from April 1980 to October 1982 and was completed in March 1983.

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ACKNOWLEDGMENT

Dr. Foppe B. DeWalle, University of Washington at Seattle, provided analytical services, technical direction and sampling equipment. The firm of Holzmacher, McLendon & Murrell, P.C. also provided analytical services.

Vincent Alonge and Erick B. Kurz, Cedar Creek Wastewater Reclamation Plant, participated in priority pollutant sample collection and trihalomethane analyses which were conducted at the Cedar Creek Wastewater Reclamation Laboratory.

Richard Cotugno and William Lahey participated in the installation and maintenance of the sampling equipment.

Cecil Lue-Hing, PRC Consoer Townsend, Jericho, New York, also participated in priority pollutant sample collection.

SECTION 1

INTRODUCTION

The groundwater aquifers which underlie Nassau County, New York, provide the sole source of potable water supply for the inhabitants of this County. Recharge of these water bearing aquifers is provided by rainfall within the water budget area of Nassau County. During the period before World War II, most homes in Nassau County utilized cesspools or septic tanks, discharging their wastewater effluents directly into the Upper Glacial Aquifer. Even in those few inland communities which provided sewage treatment, effluent disposal through leaching basins into the Upper Glacial Aquifer was the accepted practice. The rapid urbanization which took place after World War II was accompanied by increased groundwater pumping and extensive contamination of the Upper Glacial Aquifer. In many areas, these domestic discharges have resulted in pollution of the Glacial Aquifer to such an extent that nitrate and detergent levels contravene standards. In order to retard the contamination of this aquifer and to protect the remaining aquifers which provide Nassau and Suffolk Counties with their sole source of potable water supply, Nassau County embarked upon a sewer program in 1950 which, when completed in 1985, will result in 85% of the County being sewered.

An Environmental Impact Statement (EIS) on Wastewater Treatment Facilities Construction Grants for Nassau and Suffolk Counties, New York was finalized in 1972.(1) Adverse environmental effects associated with the sewer program and subsequent discharge of the treated sewage effluent into Long Island Sound, the South Shore Bays and the Atlantic Ocean could cause groundwater levels to decline, unless the decline is counterbalanced by groundwater recharge. The declining groundwater levels could result in: 1) decreased groundwater inflow to streams, 2) declining levels of "water table" lakes, 3) decreased subsurface groundwater outflow to the bays, Long Island Sound, and the Ocean, and 4) salt-water intrusion into the aquifers. These declining groundwater levels could cause increased salinity in some of Long Island's estuaries and bays, and thus alter the ecosystem of these saline water bodies.

As part of the EIS conclusions, it was determined that: 1) the construction of collection systems and effective wastewater treatment facilities are essential to protect the public water

supply of Long Island and 2) as soon as the technology is available, it would be advantageous for Long Island to implement groundwater recharge for the ultimate protection of its water supply.

A feasibility study entitled "Correlation of Advanced Wastewater Treatment and Groundwater Recharge"(2) was completed under a federal grant in August 1973. This report, after being approved by the EPA in July 1974, served as the basis for the design of the 0.24 m^3/s (5.5 mgd) Cedar Creek Wastewater Reclamation - Recharge Facilities.

The Cedar Creek Wastewater Reclamation - Recharge Facilities have been constructed and plant operations (startup April 1980) and groundwater recharge operations (startup October 1982) are underway. A primary concern from conceptual design to the present has been the production of a high quality water for groundwater recharge. During the development of water quality criteria for groundwater recharge, the New York State Department of Environmental Conservation (NYSDEC) required data that demonstrated the performance and reliability of the treatment processes before finalizing Nassau County's State Pollutant Discharge Elimination System (SPDES) permit for groundwater recharge. In addition to the State's data requirements, the EPA provided Nassau County with a grant to measure the priority pollutants in the treatment and recharge facilities. The initial results of the priority pollutants study were used in the development of the SPDES permit.

This research project was initiated with the overall objective of determining the presence and fate of priority pollutants in Cedar Creek's advanced wastewater reclamation - recharge facilities. The specific project objectives were to: 1) determine individual treatment processes' and overall treatment plant performance for the removal of priority pollutants, 2) determine the transformation or generation of priority pollutants by the treatment processes, and 3) determine the priority pollutants present in the groundwater prior to and after recharge. It was acknowledged during the planning period that the number of samples would be minimal and the results would be indicative rather than deterministic. This approach was acceptable because the facility was in its initial stages of operation and the analytical results would indicate problems rather than provide statistical evaluations of performance and reliability.

This report is a summary of an initial survey of priority pollutants as they relate to the overall plant performance, including individual unit process performance, effect of chlorination, and the effects on recharge operations. The report provides preliminary data showing that up to 72 priority pollutants are present in the influent and/or effluent and significant removal efficiencies (up to >99%) are being obtained. The

data also indicate that trihalomethanes are being formed during both the treatment and recharge operations. This finding requires further investigation although corrective measures have already been taken.

SECTION 2

CONCLUSIONS

1. The analysis of overall plant performance indicates that the Cedar Creek Wastewater Reclamation Plant (CCWRP) provides the following removals of priority pollutants, based on total mass of identified compounds:

Volatile Organics	85%
Extractable Organics	80%
Pesticides/PCBs	47%
Metals	64%

2. The concentrations of the trihalomethanes bromoform, chloroform and dibromochloromethane appear to increase in the plant effluent after chlorination.

3. Pesticides/PCBs removal efficiencies are highly dependent upon influent concentrations. A removal efficiency of 91% was achieved when the influent level was 7215 ng/l, 67% at an influent level of 1677 ng/l and essentially zero at 552 ng/l. Effluent concentrations ranged from 550 to 675 ng/l which is apparently the lowest level achievable.

4. It is difficult to draw firm conclusions regarding unit process performance for the removals of priority pollutants because the number of samples analyzed was small and many compounds were below detection levels. In a few cases, pollutant concentrations in the effluent were found to be higher than their corresponding concentrations in the influent, resulting in large variations in removal efficiencies.

5. The study indicates that primary sedimentation with lime addition effectively reduces concentrations of volatile organics and heavy metals. Removals of individual volatile organic compounds ranged up to 90% while metals removals ranged up to 79%. Primary treatment did not effectively remove phenols or cyanide.

6. Biological treatment with alum addition removed the remaining volatile organics in the primary effluent to levels below detection. Bis(2-ethylhexyl)phthalate was removed by >94% during the one event when it was detected. Biological treatment also removed 81% of the heavy metals detected and 83% of the phenol.

7. The performance of the filtration/carbon adsorption system was difficult to evaluate due to non-detectable levels of most priority pollutants.

8. The combined effect of high COD concentration and high chlorine dose appears to be significant with respect to THM formation.

9. Prior to commencement of recharge operations, low-molecular-weight hydrocarbons such as, tetrachloroethene, trichloroethene, 1,2-dichloroethene and 1,1,1-trichloroethane were detected at significant levels in a majority of observation wells. Detectable levels of heavy metals (copper, lead and zinc) and bis(2-ethylhexyl)phthalate were also observed.

10. Observation well samples taken after recharge demonstrate an increase in TTHM concentrations in the aquifer. Residual chlorine, combined with organic carbon in the recharge water and long detention times, appear to be determining factors.

SECTION 3

RECOMMENDATIONS

1. Evaluate the formation of THMs in the plant and recharge operations.

   As part of this evaluation:

   a) optimize chlorine dose to reduce residual chlorine levels;

   b) investigate the use of alternative disinfectants, such as chlorine dioxide or ozone;

   c) identify and reduce THM precursors; and

   d) increase the organics removal efficiency of the carbon adsorbers by increased carbon regeneration frequency, or increased contact time.

2. More sensitive analytical protocols than standard EPA methods, e.g. XAD resin concentration, should be used for future investigations of unit process removals of priority pollutants.

SECTION 4

DESCRIPTION OF CEDAR CREEK WASTEWATER RECLAMATION PLANT AND RECHARGE FACILITIES

RECLAMATION PLANT

Background

The Cedar Creek Wastewater Reclamation Plant (CCWRP) is an advanced wastewater treatment (AWT) plant consisting of grit removal, chemically aided primary clarification, suspended growth nitrification/denitrification, chemically aided sedimentation, dual-media filtration, carbon adsorption and chlorine disinfection. The CCWRP was constructed on the site of the Cedar Creek Water Pollution Control Plant (CCWPCP) and was designed to produce an effluent suitable for groundwater recharge at an influent flow rate of 0.24 m^3/s (5.5 mgd). The effluent from the reclamation plant is transported 10.1 km (6.5 miles) northwest of the plant, via a 610 mm (24 inch) diameter concrete lined steel pipe, to the Cedar Creek Recharge Facilities in East Meadow, New York.

The basic approach taken for design of the CCWRP was the incorporation of the best available technology in 1974, combined with the maximum utilization of the existing plant facilities. Modifications to existing facilities include the following: 1) flocculation chambers were constructed by placing a bulkhead and horizontal shaft, slow speed, turbine mixers in the influent channel to two of the six existing primary tanks; 2) two of the twelve existing aeration tanks and one of the eight final clarifiers were used for combined carbon oxidation-nitrification; 3) two aeration tanks and a final clarifier were used for denitrification-post aeration; 4) two aeration tanks and the existing chlorine handling equipment were used for disinfection; and 5) existing solids handling facilities were utilized. New processes and equipment included: 1) rapid mix basin and chemical handling systems for lime slaking, ferric chloride, polymer, and alum; 2) gravity flow, mixed-media filters; 3) gravity flow, granular activated carbon adsorbers; 4) carbon regeneration furnace; and 5) methanol feed system.

Since the filters, carbon adsorbers, and carbon regeneration system were designed for full scale operation, these units can be utilized in an area-wide reclamation program for Nassau

County, thus extending the service life of the equipment and further increasing the returns on the demonstration program expenditures.

The following sections provide brief desciptions of the treatment processes employed at the CCWRP as depicted in Figure 1.

Preliminary Treatment and Grit Removal

The CCWPCP provides facilities for preliminary treatment (bar screens and comminutors) and grit removal. The grit chamber effluent flows by gravity to primary treatment, where the flow is split: a constant 0.24 m^3/s to the CCWRP and the remainder of the flow to the CCWPCP.

Chemically Aided Primary Treatment

The primary treatment system employs the addition of lime followed by primary sedimentation to aid removal of phosphorus, biochemical oxygen demand (BOD), suspended solids and heavy metals, thereby optimizing and protecting the biological nitrification system. Lime is added at an average dosage of 105 mg/l, which increases the pH of the wastewater to a range of 9.0 to 9.3.

The degritted wastewater is conveyed to chemical treatment facilities which consist of an automatic lime feed system including a slaker, slurry tank and feed pumps, and a rapid mix tank for chemical dispersal. The effluent from the rapid mix tank is discharged by gravity to two flocculation chambers, each containing a horizontal shaft, slow speed mixer. The flocculated effluent then flows to one of two primary sedimentation tanks.

Two Stage Biological Treatment

The secondary treatment system is designed to promote biological nitrogen removal in conjunction with oxidation of carbonaceous material. The design allows for the operation of the secondary system as a two stage suspended growth system. Combined carbon oxidation-nitrification with intermediate clarification is followed by methanol aided denitrification, post aeration-stabilization and final clarification.

Effluent from the primary sedimentation tank flows by gravity through the carbon oxidation-nitirification tank which provides a detention time of 5.9 hours based on the design flow rate. From the combined carbon oxidation-nitrification tank, the mixed liquor enters a 30.5 m diameter clarifier. Sludge from this intermediate clarifier (CCWPCP Final Tank No. 5) is returned to the carbon oxidation-nitrification tank and excess sludge is wasted to the CCWPCP solids handling facility, which

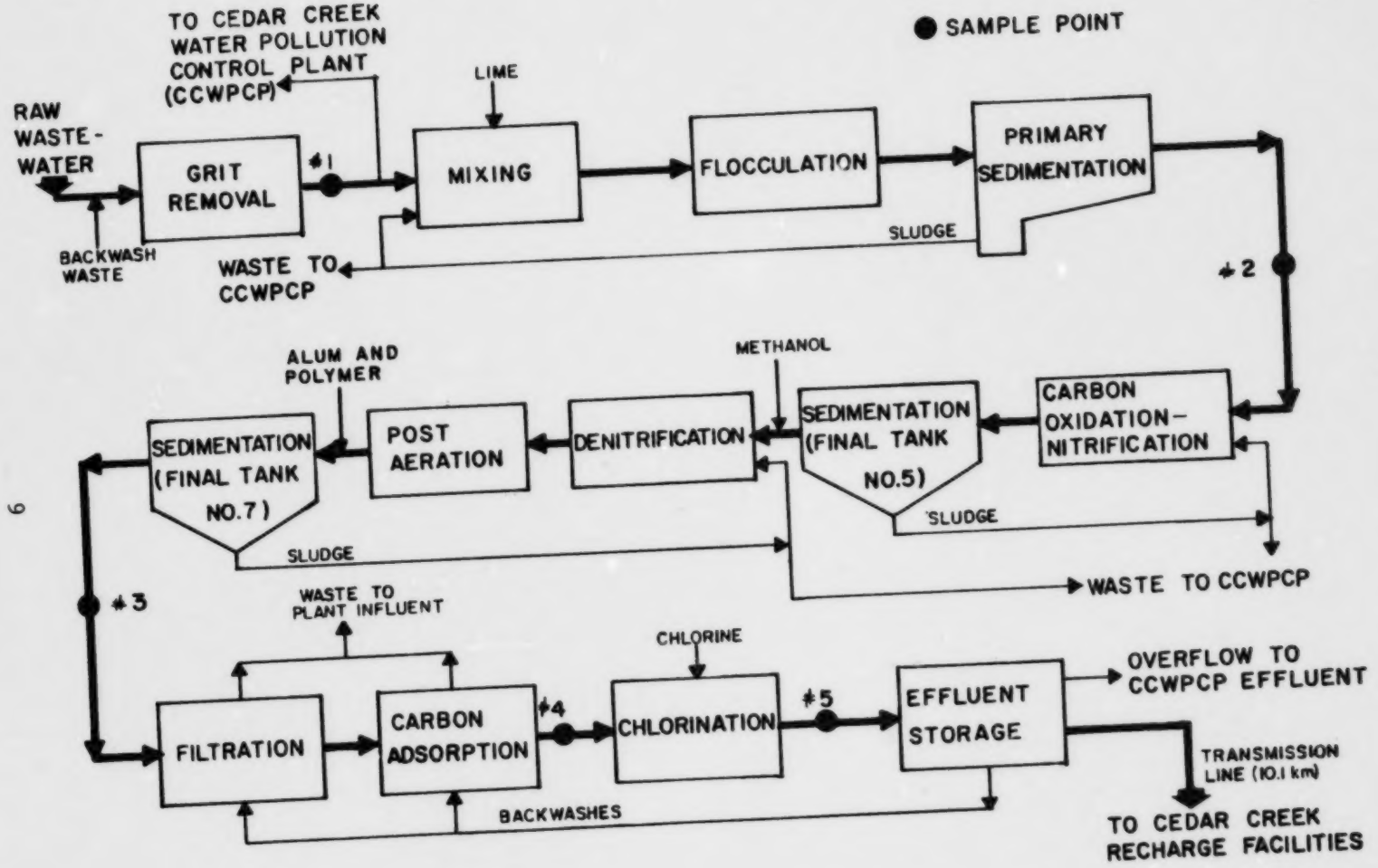

Figure 1. Cedar Creek Wastewater Reclamation Plant.

consists of dissolved air flotation, anaerobic digestion, and ocean disposal.

The nitrified effluent from the intermediate clarifier flows to the denitrification tank, which provides a detention time of 2 hours. Methanol is added at the tank influent at a controlled rate (average methanol to nitrate ratio of 3.5) as a supplemental organic carbon source in the denitrification process.

The denitrified liquor flows to a post aeration-stabilization tank. The purpose of this tank is to: 1) remove any supersaturated nitrogen gas; 2) minimize rising sludge problems in the final clarifier; and 3) provide an additional aeration period for the removal of excess methanol. The aerated liquor is conveyed to a second clarifier (CCWPCP Final Tank No. 7) for final clarification using alum and polymer additions at average dosages of 45 mg/l and 0.7 mg/l, respectively.

Operational flexibility is provided to allow conversion from a two stage to a three stage biological treatment system, in order to assure the production of a high quality effluent. A three stage intermediate system would consist of a high rate carbon oxidation unit followed by separate nitrification and denitrification steps.

Filtration and Carbon Adsorption

The clarified effluent from the biological system is pumped to four parallel operated, dual-media, gravity filters. Two filters are provided in service with two additional filters on standby. Each filter provides a surface area of 47.8 m^2 and operates at a surface loading rate of approximately 2.7 $l/m^2/s$.

The filtered effluent flows to the carbon adsorption system, which consists of two gravity units operated in parallel, with two standby units. The adsorption units are operated in a down-flow packed bed mode. Each unit provides 47.8 m^2 of surface area with a 2.4 m bed depth, a surface loading rate of 2.7 $l/m^2/s$, and a contact time of approximately 0.27 hours.

Chlorination and Storage

Two of the aeration tanks at the CCWPCP were covered and serve as the chlorine contact chamber and effluent storage tank for the CCWRP. The adsorber effluent is pumped to the chlorine contact chamber, which provides a 0.5 hour detention period. The chlorinated effluent is then discharged to a 6,056 m^3 effluent storage clear well which provides sufficient detention time (approximately 7 hours) for disinfection of the CCWRP effluent and provides the necessary storage of backwash water for the filters and carbon adsorbers. This clear well also serves as a pump suction chamber for the transfer pumps which

deliver the treated effluent, via a 10.1 km, concrete lined steel pipe, to the recharge facilities.

RECHARGE FACILITIES

Background

Long Island is underlain by consolidated bedrock which, in turn, is overlain by a wedge-shaped sequence of unconsolidated sedimentary rocks. The top of the bedrock, which is about 61 m below sea level in the northwestern part of Nassau County, slopes to the southeast to a depth of about 518 m below sea level in the southeast corner of the county. The average slope of the bedrock surface is about 0.02 percent.

The unconsolidated sediments that overlie the bedrock consist mostly of glacial deposits of Pleistocene age and fluvial deltaic deposits of Cretaceous age. The sediments of both ages are composed of gravel, sand, silt, clay and mixtures thereof. The cretaceous deposits were eroded by streams and glaciers, and the Pleistocene sediments were, therefore, deposited on an irregular surface that locally was characterized by moderate relief.

The most important hydrogeologic units related to artificial recharge in Nassau County are the Upper Glacial Aquifer and the Magothy Aquifer. The Upper Glacial Aquifer forms the surficial cover throughout most of Nassau County. Water from precipitation and other sources applied on the land surface moves downward to the water table and then moves either laterally in the Upper Glacial Aquifer or downward to the Magothy Aquifer, depending on hydraulic gradients and the permeability of the materials. Most of the groundwater for public supply in Nassau County is withdrawn from the Magothy Aquifer. Recharge to the Magothy is virtually all through percolation from the overlying Upper Glacial Aquifer.

The Recharge Facilities consist of recharge basins, injection wells, a storage reservoir, and associated equipment required for the recharge of water from the CCWRP. The East Meadow recharge site is located on a triangular piece of county owned land at the approximate geographic center of Nassau County. The site is occupied in part by the Nassau County Correction Center Vegetable Farm and by the structures and leaching basins of the abandoned Meadowbrook Sewage Treatment Plant.

The Meadowbrook Sewage Treatment Plant was phased out in 1975. The facility was a 0.01 m^3/s secondary treatment plant using trickling filters which, prior to 1956, discharged treated effluent to the groundwater through leaching fields. The past operations of the nearby sewage leaching fields makes the

current recharge site less than optimum for evaluation of groundwater quality during recharge with AWT effluent, although further degradation of the groundwater quality is less likely due to these past operations.

Water to be recharged is received into a 144 m^3 central reservoir from where it is distributed to the wells and basins. The reservoir provides 0.17 hours detention at the design flow rate of 0.24 m^3/s. Pumping facilities are provided in the Operations Building, along with a sodium hypochlorite feed system which can be used, if required, to control biological activity in the recharge basins. Flow rates, line pressures, and recharge water quality are monitored and controlled at this building. A schematic of the Recharge Facilities is presented in Figure 2.

Recharge Basins

Ten basins are provided at the recharge site. Basins numbered 1 through 7 are 1.52 m deep and were constructed to evaluate: 1) the most effective procedures in optimizing the recharge rate; 2) the causes of clogging of the basin floor; and 3) the ability of the unsaturated soil zone to improve the quality of the percolating reclaimed wastewater. The operation of each of these seven basins will be varied by the use of several application-rest schedules and by the use of various basin floor treatment methods. It is anticipated that initial basin infiltration rates will range between 0.15 and 0.45 m/d and that application-rest schedules will be established only after each basin has been fully characterized during initial recharge operations.

Basins 2 and 3 have been specifically designed and constructed to examine the unsaturated soil zone during recharge (the top of the Upper Glacial Aquifer is located 9.1 m below the floor of each basin). Each of these basins has a 1.8 m retaining wall and contains a 3.7 m diameter observation manhole that extends 4.9 m below the basin floor.

Basins 8, 9 and 10 were part of the Meadowbrook Sewage Treatment Plant leaching field. Basin 8 is a 4.6 m deep pit designed to evaluate the effectiveness of recharge through deep basins while Basins 9 and 10 are 1.5 m deep and will be used to accommodate water in excess of that required to operate Basins 1 through 8.

Stormwater Basin 62 is presently being used for the recharge of storm runoff. This basin can also be used for the emergency disposal of reclaimed water. Whenever sufficient water is available, studies may be conducted in the recharge basin itself to evaluate the effectiveness of using storm runoff basins for the supplemental recharge of reclaimed wastewater.

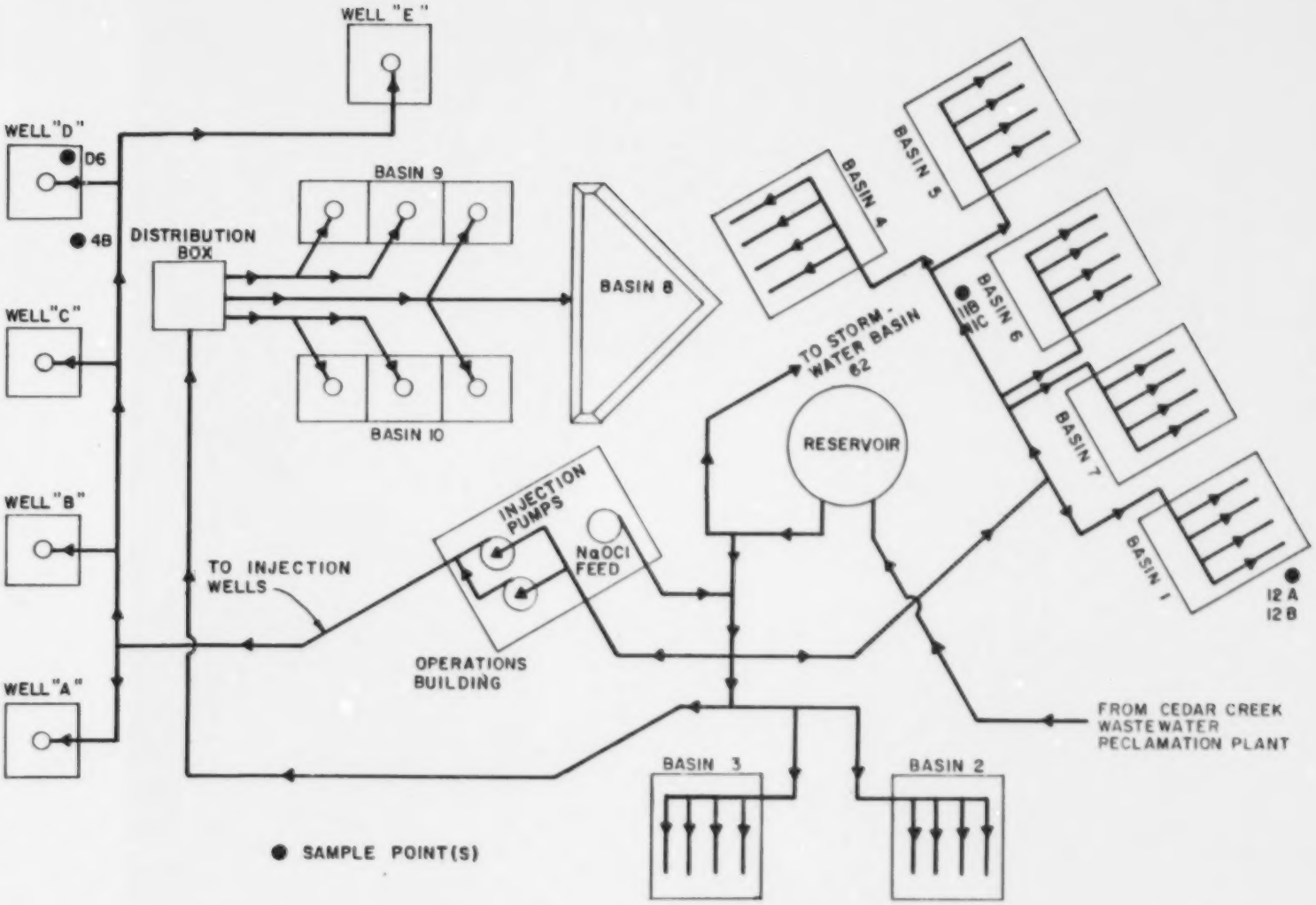

Figure 2. Cedar Creek Wastewater Recharge Facilities

Injection Wells

Five shallow injection wells are provided near the western border of the site. Four wells are artificial gravel pack wells; that is, they were constructed with a fine gravel filter pack between the well screen and aquifer material. The fifth well is a natural gravel pack well; that is, it was constructed so that the well screen is in direct contact with the aquifer material. Each well extends 30.5 m below the land surface and is screened between a depth of 22.9 to 29.0 m below land surface. Recharge will be through four wells at any given time, with one well in standby. An injection rate of 0.022 m^3/s (0.5 mgd) per well will be maintained for a total recharge through the wells of 0.088 m^3/s (2 mgd).

Observation Wells

In addition to the two 4.9 m deep observation manholes located in Recharge Basins 2 and 3, the East Meadow recharge site is surrounded by a network of 42 observation wells located at 20 sites. The groundwater observation wells extend to depths of 15.2 m (upper portion of the Upper Glacial Aquifer), 30.5 m (base of the Upper Glacial Aquifer) and 61.0 m (upper portion of the Magothy Aquifer) and have been installed in the direction of groundwater flow.

The purpose of the observation wells and manholes is to provide adequate sites for the collection of groundwater samples before, during and after recharge so that the impact of the recharge operation on the groundwater can be adequately studied.

PLANT EFFLUENT AND DISCHARGE PERMIT CRITERIA

Table 1 presents the anticipated water quality of raw wastewater and effluent at various stages of treatment in the CCWRP based on the system's design.(2) Estimated concentrations for wastewater constituents are presented for the raw wastewater through various stages of treatment, up through the chlorination process. Omitted constituent data are not applicable.

Tables 2 and 3 summarize effluent limitations and monitoring requirements as set forth by the New York State Department of Environmental Conservation (NYSDEC) in the CCWRP's State Pollution Discharge Elimination System (SPDES) permit, issued in July 1982. Discharge limitations are presented in terms of daily maximum concentrations for both individual constituents and specified aggregates. Monitoring frequencies and sample types are described in Table 3. These standards and requirements can be modified to incorporate other organics and/or inincrease the frequency of monitoring.

TABLE 1. ANTICIPATED WATER QUALITY THROUGH TREATMENT PROCESSES AT THE CCWRP*

Constituent	Raw Wastewater Concentration	Primary Clarifier	Carbon Oxidation Nitrification	Denitrification Post Aeration	Filtration	Carbon Adsorption	Chlorination
BOD	200	80-100	5-15	4-8	1-5	0-2	
COD	350	150-250	60-85	40-60	30-50	10-25	
TOC	130		10-20	10-20	10-15	5	
NH_3-N	22	18	0-2	0-1	0-1	0-1	
NO_2+NO_3-N			20	0-1	0-1	0-1	
Organic N	13	7	1-2	1-2	1-2	1-2	
Total N	35	25	21-24	2-3	2-3	2-3	
Ortho PO_4 as P	10	1-4	1-3	0.1-0.3	0.1-0.2	0.1-0.2	
Total PO_4 as P	16	2-4	1-3	0.1-0.3	0.1-0.2	0.1-0.2	
Turbidity, JTU	250			10-20	0.1-2	0.1-1	
TSS	200	50-70		4-10	1-3	1-2	
TDS	500			350-450			350-500
Hardness as $CaCO_3$	120						
Alkalinity as $CaCO_3$	190						
F	0.5				0.25-0.5	0.25-0.5	
Cl	60-75						70-80
SO_4	70						70-90
pH, std. units	7.4						6.5-8.5
MBAS	10.0			0.3-1.5			0.03-0.3
CCE	8.0			1.6			0.05-0.5
Phenols	0.15						0.005
Coliform per 100 ml	50 x 10^6						2
Al	0.7		0.5-1		0.02-0.03	0.01-0.02	
As			0.01				
Ba	0.2		0.007				
B	0.3		0.8-1.2		0.3-0.5	0.3-0.5	
Cd	0.01		0.01				
Cr(+6)			0.01-0.03		0.01	0.01	
Cr(total)	0.9		0.3-0.5		0.3-0.5	0.3-0.5	
CN	0.04		0.03-0.07		0.01	0.01	
Fe + Mn	2.0		0.2-0.7		0.07-0.4	0.07-0.4	
Pb	0.2		0.06-0.08				
Hg	0.001		0.0005				
Se	0.02		0.005-0.01				
Ag	0.01		0.005				
Zn	0.7		0.2-0.25				

*All values in mg/l unless otherwise noted.

TABLE 2. SPDES FINAL EFFLUENT DISCHARGE LIMITATIONS

Effluent Parameter	Discharge Limitations (Daily Max.)
Metals	**mg/l**
Antimony	0.05
Arsenic	0.025
Barium	1.00
Beryllium	0.20
Cadmium	0.01
Chromium - total	0.5
Colbalt	1.00
(1) Iron	0.30
Lead	0.025
(1) Manganese	0.30
Mercury	0.002
Nickel	2.0
Selenium	0.01
Silver	0.05
Thallium	0.02
Zinc	0.30
Copper	0.20
Volatile Organics	**ug/l**
(2) Dichlorofluoromethane	50.0
Chloroethene	1.0
(2) Dichloromethane	50.0
(2) 1, 2 Dichloroethene	1.0
(2) 1, 1 Dichloroethane	50.0
(2) Trichloromethane	10.0
(2) 1, 1, 1 Trichloroethane	50.0
1, 2 Dichloroethane	2.0
(2) Tetrachloromethane	0.3
Benzene	(9)
Trichloroethene	5.0
(2) Bromodichloromethane	50.0
(5) Methylbenzene	50.0
(2) Dibromochloromethane	50.0
Tetrachloroethene	10.0
(3) Chlorobenzene	10.0
(5) Ethylbenzene	50.0
(2) Tribromomethane	50.0
Chlorinated Compounds	**ug/l**
Alpha BHC	0.2
Beta/gamma BHC	0.2
Delta BHC	0.2
Heptachlor	(9)
Aldrin	(9)
Dieldrin	(9)
Heptachlorepoxide	(9)
(4) P, P' - DDE	0.1
Endrin	(9)
Beta-endosulfan	5.0
(4) P, P' - DDD	0.1
Endrin aldehyde	(9)
Endosulfan sulfate	5.0
(4) P, P' - DDT	(9)
(4) P, P' - DDT	(9)
Mirex	0.1
Alpha Chlorodane	0.03

Effluent Parameter	Discharge Limitations (Daily Max.)
Base/Neutral/Acid Compounds	**ug/l**
Bis (chloroethy) lether	0.09
(3) 1, 4 Dichlorobenzene	10.0
(3) 1, 2 Dichlorobenzene	10.0
Nitrobenzene	30.0
Bis (2-chloroethoxy) methane	2.0
(6) Naphthalene	30.0
(6) 2-Chloronaphthalene	10.0
(6) Acenaphthylene	10.0
(7) Diethylphthalate	50.0
2, 6 Dinitrotoluene	50.0
(6) Fluorene	10.0
(7) Diethylphthalate	50.0
Azobenzene	1.0
N-Nitrosodiphenylamine	14.0
(6) Phenanthrene	10.0
(6) Anthracene	10.0
(7) Di-n-butylphthalate	50.0
(6) Fluoranthene	0.2
(6) Pyrene	0.2
(7) Butylbenzylphthalate	50.0
(7) Bis (2-ethylhexyl) phthalate	75.0
(7) Di-n-octylphthalate	50.0
(3) 1, 3 Dichlorobenzene	10.0
N-Nitrosodiphenylamine	14.0
(8) Phenol	1.0
(8) 2, 4 Dimethylphenol	1.0
(8) 4-Chloro, 2-methylphenol	1.0
(8) 2, 4, 6 Trichlorophenol	2.0
(8) 2-Nitrophenol	1.0
(8) 2, 4 Dichlorophenol	1.0
(6) Acenaphthene	10.0
Misc. Chemical	**mg/l**
Ammonia	2.0
Chloride	250.0
Fluoride	1.5
Nitrates + Nitrites	10.0
Cyanide	0.2
Chlorine Residual - Free	5.0
Sodium	170.0
Oil and Grease	15.0
pH	(10)
Physical	
Turbidity	5 NTU
Color	15 Units
TDS	1,000 mg/l
Flow	4.0 MGD
Microbiological	
Virus	(11)
Coliform	1/100 ml

NOTES:

(1) to (8) Total aggregate concentration of these constituents shall not exceed: (1) 0.50 mg/l, (2) 50.0 ug/l, (3) 10.0 ug/l, (4) 0.1 ug/l, (5) 50 ug/l, (6) 30 ug/l, (7) 75 ug/l, nor (8) 1.0 ug/l.

(9) Not detectable by tests or analytical determination references in 6 NYCRR 703.4.

(10) The pH shall not be less than 6.5 standard units nor greater than 8.5 standard units.

(11) No viral standard has been set, although analyses must be conducted on a weekly basis.

TABLE 3. FINAL EFFLUENT MONITORING REQUIREMENTS

Parameter or Parameter Group	Measurement Frequency	Sample Type
Metals	Weekly	24 hr. composite
Volatile Organics	Weekly	Grab
Base/Neutral/ Acid Compounds	Monthly	Grab
Chlorinated Compounds	Monthly	Grab
Misc. Chemical		
Ammonia	Weekly	24 hr. composite
Chloride	Weekly	24 hr. composite
Fluoride	Weekly	24 hr. composite
Nitrates + Nitrites	Weekly	24 hr. composite
Cyanide	Weekly	24 hr. composite
Chlorine Residual - Free	Daily	Grab
Sodium	Weekly	24 hr. composite
Oil and Grease	Weekly	24 hr. composite
Physical		
Turbidity	Daily	Grab
Color	Monthly	Grab
TDS	Daily	Grab
Flow	Daily Avg.	Continuous
Microbiological		
Coliform (Total)	Daily	Grab
Virus	Weekly	Grab

SECTION 5

PLANT PERFORMANCE IN REMOVING CONVENTIONAL POLLUTANTS

BACKGROUND

An analysis of conventional pollutants removal was conducted in order to evaluate the past performance and reliability of the CCWRP. Daily operating data for the first 15 months of continual operation (October 1980 to December 1981) were analyzed using the lognormal frequency distribution model and the results are summarized in this section.

Table 4 presents the effluent concentrations and removal efficiencies of the major conventional pollutants at various stages of treatment. In addition, the overall reliability of the plant, defined as the measure of the degree of successful performance with respect to either the maximum anticipated effluent concentration for a given process or the maximum effluent discharge limitation(s), is also presented.

The reliability of an individual unit process is expressed as the percent of time that an expected effluent concentration is achieved for the appropriate constitutents presented in Tables 1 and 2. Overall plant reliability is similarly expressed; however, two values were established for each appropriate constituent, based on two independent criteria: 1) the expected plant effluent concentration and 2) the corresponding SPDES limitation.

BIOCHEMICAL OXYGEN DEMAND (BOD)

Plant BOD removal, as determined by the standard 5-day test, is greater than 99%, based on geometric mean influent and effluent values. The chemically aided primary sedimentation tank exhibits an average BOD removal of 46%. BOD removal through biological treatment (Final Tank No. 7) averages 98%, with additional removals across the filters and carbon adsorbers.

The overall plant performance meets the maximum anticipated BOD value of 2 mg/l 95% of the time with a final effluent geometric mean concentration of 0.65 mg/l. Thus, the reclamation plant achieves the anticipated level of performance.

TABLE 4. REMOVAL OF CONVENTIONAL POLLUTANTS THROUGH THE CCWRP

Constituent	Parameter	Raw Wastewater	Primary Effluent	Final Tank No. 5 Effluent	Final Tank No. 7 Effluent	Plant Effluent	Anticipated Effluent	Plant Reliability %
BOD	M	190	102		4.4	0.65	0-2	95
	n	434	433		434	346		
	95% CI	184-196	100-104		4.2-4.6	0.6-0.7		
	% Rem.		46		98	>99		
COD	M	388	214	28.7	26.4	8.3	10-25	95
	n	352	426	426	428	398		
	95% CI	382-394	210-217	28-30	26-27	7.7-8.9		
	% Rem.		45	93	93	98		
TSS	M	179	84	13.4	20.2	1.6	1-2	64
	n	450	442	434	445	379		
	95% CI	175-183	82-86	13-14	19-21	1.5-1.7		
	% Rem.		53	93	89	>99		
PO_4-P	M	6.6	4.4		0.9	0.19	0.1-0.2	52
	n	352	345		310	313		
	95% CI	6.4-6.7	4.2-4.6		0.84-0.96	0.17-0.22		
	% Rem.		33		86	97		
NH_3-N	M	23.7	22.4	0.46	0.62	0.52	2†	94
	n	373	367	371	369	279		
	95% CI	23.5-24.0	22.1-22.7	0.41-0.52	0.56-0.68	0.47-0.58		
	% Rem.		5	98	97	98		
NO_3-N	M			13.8	0.26	0.30	10†	>99
	n			366	366	272		
	95% CI			13.4-14.1	0.24-0.30	0.24-0.36		
	% Rem.				98	98		
Org. N	M	11.2	8.3	0.66	0.70	0.22	1-2	98
	n	311	304	281	285	116		
	95% CI	10.0-11.5	8.1-8.6	0.58-0.74	0.63-0.78	0.17-0.27		
	% Rem.		26	94	94	98		

† SPDES Permit effluent limitations.
M - Geometric mean concentration in mg/l
n - Number of data points
95% CI - 95% confidence interval for M
% Rem. - Cumulative % removal

CHEMICAL OXYGEN DEMAND (COD)

COD removal across the primary sedimentation tank shows an average removal of 45%, based on geometric mean values. Cumulative COD removal through biological treatment averages 93%. Overall COD reduction through filtration and carbon adsorption averages 98%, resulting in an effluent COD level of 8.3 mg/l. The overall plant performance meets the maximum anticipated COD value of 25 mg/l 95% of the time.

It should be noted that due to the poor lognormal fit of the plant effluent data, these values are only reasonable estimates of the true values. However, it appears that the COD removal performance achieved by the reclamation plant is greater than anticipated.

TOTAL SUSPENDED SOLIDS (TSS)

TSS removal across the primary sedimentation tank averages 53%. The mean effluent TSS concentrations from the intermediate (Final Tank No. 5) and final settling tanks (Final Tank No. 7) are 13.4 mg/l and 20.2 mg/l, respectively, indicating poor performance of Final Tank No. 7. Inferior performance resulted from high solids loadings and the need to optimize alum and polymer dosages.

The filtration and carbon adsorption processes reduce the remaining TSS to a mean level of 1.6 mg/l with a reliability of 64% for the anticipated value of 2 mg/l. Although plant performance is in the range anticipated, it appears that the reliability of suspended solids removal by the reclamation plant can be further increased by improving the performance of Final Tank No. 7.

PHOSPHORUS (TOTAL PO_4 AS P)

The mean measured influent phosphorus level of 6.6 mg/l is approximately 60% lower than the design value of 16 mg/l. This reduction is most likely due to an industry reduction of phosphate levels in detergents placed into effect after completion of the design. Primary sedimentation with lime addition reduces this level to 4.4 mg/l, resulting in an average removal of 33%. Further phosphorus reduction is achieved through biological treatment, and alum precipitation in Final Tank No. 7, to a mean of 0.9 mg/l as compared with the anticipated level of 0.3 mg/l.

Overall phosphorus reduction through filtration averages 97%, producing a mean effluent concentration of 0.19 mg/l. Although the mean effluent phosphorus concentration falls within

the anticipated design range, final effluent phosphorus levels are less reliable (52%) than those of the other conventional pollutants.

AMMONIA (NH_3-N)

Nitrogen in the plant influent is essentially in the forms of ammonia and organic nitrogen. Oxidation of ammonia nitrogen to nitrate nitrogen is accomplished in the combined carbon oxidation-nitrification process (98% removal). The plant effluent ammonia concentrations have a geometric mean value of 0.52 mg/l. The maximum daily concentration (SPDES permit) for ammonia in the plant effluent in 2 mg/l. The CCWRP achieved this requirement 94% of the time. Again, this value is only a reasonable estimate of the true value, due to the marginal log-normal fit of the plant effluent data.

NITRATE (NO_3-N)

Nitrate nitrogen generated during the nitrification process of ammonia is removed via the dentrification process. Dentrification removed approximately 98% of the nitrate nitrogen. The geometric mean nitrate concentration in the plant effluent is 0.26 mg/l. The maximum daily discharge limitation for nitrate and nitrite is 10 mg/l. Since the nitrite concentration is very low (<0.01 mg/l), the CCWRP should achieve this requirement greater than 99% of the time, on a daily basis. Inspection of the data shows that only one value, from a sample size of 369, was greater than 10 mg/l.

ORGANIC NITROGEN

Organic nitrogen in colloidal or suspended form is removed by physical entrapment, either by settling or filtration. Soluble organic nitrogen in the plant influent will be biologically hydrolyzed to ammonia before oxidation in the nitrification process. Chemically aided primary sedimentation removes 26% of the influent organic nitrogen. The overall average organic nitrogen removal through the nitrification process is 94%. The cumulative reduction in organic nitrogen concentrations across the plant is 98%, characterized by a mean effluent concentration of 0.22 mg/l, with a reliability of 98%.

SECTION 6

PRIORITY POLLUTANTS AND OTHER TRACE CONTAMINANTS IN THE PLANT AND PROCESS EFFLUENTS

SAMPLING PROCEDURES

The sampling and analysis program for priority pollutants was divided into three phases. The first phase was conducted during April, May and June, 1981 in order to determine the overall performance of the CCWRP. The second phase, conducted during August, September and October, 1982, was designed to investigate the performances of individual CCWRP processes. The third phase involved the analyses of samples taken from monitoring wells at the recharge facility site. These samples were collected in May and October, 1982, to determine the effect of recharge on groundwater below the site. The sampling points out the dates samples were taken and are shown in Table 5.

A total of 37 samples were collected over the project period. The sample location identification numbers delineated in Table 5 are indicated schematically in Figures 1 and 2, which depict the reclamation and recharge facilities, respectively.

Plant Sampling

The plant influent was sampled at the effluent channel from the CCWPCP grit tanks. Samples were collected at this location (ID #1) during the first phase of testing to evaluate overall plant performance and during the second phase to evaluate primary treatment performance. The primary sedimentation tank effluent (ID #2) was sampled during Phase II, only, to evaluate both primary treatment and biological treatment performances. Final Tank No. 7 effluent (ID #3) was sampled during Phase II to evaluate both biological treatment and filtration/carbon adsorption. Likewise, the carbon adsorber effluent (ID #4) analyses were used to evaluate filtration/carbon adsorption and chlorination. Finally, the plant effluent (ID #5) was sampled after chlorine contact but prior to effluent storage during both the first and second phases of testing. Sample analyses were used to evaluate overall plant performance and the effect of chlorination on the plant effluent quality.

TABLE 5. PRIORITY POLLUTANT SAMPLING SCHEDULE FOR THE CCWRP AND RECHARGE FACILITIES*

Date	Primary Influent I.D. #1	Primary Effluent I.D. #2	Final Tank No. 7 Effluent I.D. #3	Carbon Adsorption Effluent I.D. #4	Chlorination Effluent I.D. #5
Phase I**					
4/6/81	x				x
5/19/81	x				x
6/29/81	x				x
Phase II†					
8/19/82				x	x
9/11/82				x	x
9/28/82	x	x			
10/5/82		x	x		
10/8/82			x	x	
10/13/82				x	x
10/14/82	x	x			
10/15/82		x	x		
10/26/82			x	x	
10/27/82			x	x	
10/29/82	x	x	x		

	Monitoring Wells					
Phase III‡	4B	D6	11B	11C	12A	12B
5/11/82	x	x	x	x	x	x
10/29/82				x		x

* Location ID Nos. 1 thru 5 (see Figure 1) were 24-hour composite sampled. Monitoring wells (see Figure 2) were grab sampled.
** Analytical results presented in Tables 7, 8 and 9.
† Analytical results presented in Tables 10a and 10b.
‡ Analytical results presented in Table 11.

Plant samples were 24-hour composites started at intervals that compensated for the detention times in the various treatment units. This was done to approximate the same water mass at each location. Composite samplers were operated at constant flow rates, paralleling the constant flow rate of the AWT plant. Samples were preserved in accordance with EPA recommendations and shipped to laboratories for immediate analyses.(3)

Monitoring Well Sampling

Observation wells sampled during the third phase of this program - 4B, D6, 11B, 11C, 12A and 12B - were selected on the basis of proximity to individual recharge facilities and the direction and depth of the recharged water flow. Wells 4B and D6 were constructed to monitor the injection wells at a screened depth of 12.2 to 13.7 meters below grade. Well site 11 is located near recharge basins 4, 5 and 6 and contains three nested observation wells: well 11C at a screened depth of 12.2 to 13.7 meters, well 11B at 30.5 to 32.0 meters and well 11A, which was not selected, at 61.0 to 62.5 meters. Similarly, well site 12 contains two nested wells, 12B at 12.2 to 13.7 meters and 12A at 30.5 to 32.0 meters. Observation wells 4B, D6, 11B and 12A were not sampled after recharge because the recharged wastewater had not yet reached these wells, according to conductivity tests performed by the U. S. Geological Survey (USGS). All observation well samples were grab sampled, on the dates shown in Table 5, using a USGS specified well pump and teflon tubing. Purging time was based on the water level in the well so that stagnant water was not sampled. Samples were preserved in accordance with EPA recommendations, and shipped to laboratories for immediate analyses.(3)

Composite Samplers

Composite samples were collected using custom-made glass/teflon composite samplers designed and fabricated by D. C. Tigwell Associates of Houston under the direction of Dr. F. B. DeWalle of the University of Washington.(4) The samplers utilize glass syringes to withdraw liquid samples for analysis. After a sample is withdrawn, a teflon solenoid valve closes the intake line and opens the discharge line, emptying the contents of the syringes into a collection vessel. Each sampler is equipped with four parallel sampling trains, permitting simultaneous collection of four individual samples for subsequent analyses of volatiles, extractables, heavy metals and conventional pollutants. Volatile organics are collected in a glass cylinder equipped with a teflon float to prevent evaporation, while the extractable organics are collected in a silanized 3.78 liter (1 gallon) container.

ANALYTICAL PROCEDURES

Samples were analyzed for a total of 128 priority pollutants (asbestos was excluded), consisting of 31 volatile organics, 47 base/neutral extractable and 11 acid extractable organics, 25 pesticides/PCBs, 13 metals and total cyanide. Analyses were also performed to determine concentrations of non-priority organic pollutants.

Analyses for priority pollutants were conducted by two laboratories. Analyses for the initial six samples collected on April 6, May 9, and June 29, 1981 to provide an indication of plant influent and effluent concentrations were conducted at the University of Washington at Seattle. The results of the laboratory analyses were included in a progress report entitled "Progress Report I For Priority Pollutants in Cedar Creek Advanced Wastewater Treatment Plant Effluent, October 1981."(5) Analyses of the other 31 samples, collected in 1982 for the evaluation of the individual processes and the effect of recharge, were conducted by Holzmacher, McLendon & Murrell, P.C. (H2M) of Melville, New York.

University of Washington

Volatile organics were determined using a model 767SA purge and trap sampler (Hewlett Packard, Palo Alto, California), a model 5840 gas chromatograph (GC) and a model 4023 mass spectrometer/data system (MS/DS) (Finnegan, Sunnyvale, California) using a 15 minute purging time. After adsorption of the volatiles onto the tenax trap, the volatiles were desorbed and condensed at the front end of a liquid nitrogen cooled capillary column. The extractables were concentrated from the sample with vapor-vapor extraction using methylene chloride as the solvent. After reduction of the extract volume, a clean-up procedure utilizing gel permeation chromatography (Biobeads S-X2) was performed to remove macromolecules and lipids, and florisil adsorption chromatography was utilized to separate organics according to their hydrophobic character. Phenols were removed from the neutral fraction using cesium hydroxide modified silica gel and analyzed without derivatization using fused silica capillary columns.

The identified compounds were quantified using deuterated organics spiked into the sample before GC/MS/DS analysis. The organics D_8-toluene, D_6-2,2 dichloropropane, D_6-benzene, D_5-chlorethane, D_1-chloroform, and D_1-bromoform were used to calculate the recovery of volatile organics. The compounds D_8-naphthalene, D_{10}-phenanthrene and D_{12}-perylene were used to simulate recovery of the neutral organics. Pentafluorophenol and technazine were used as internal standards for the phenols and pesticides, respectively.

The chlorinated herbicides and pesticides were detected using a gas chromatograph equipped with an electron fix capture detector. Since gas chromatographic identification is based on elution time and comparison with a standard, it is, therefore, much less certain than the mass spectral identification used for the neutrals. Due to overlapping peaks and a shifting base line, quantification is also less reliable.

Due to the anticipated low concentrations of organics in the plant effluent, a method of concentrating organics within the sample was tested. During the first phase of the program, a polystyrene resin (XAD-2) was used to concentrate organics present in the April 6, 1981 plant effluent sample. In performing this column test, a sample volume of 143 liters was pumped through 118 grams of resin during a three day period, resulting in an empty bed contact time of 3.7 minutes. The organics were then eluted from the resin and the concentrate was analyzed for extractable organics using methods described above. Quality control methods are cited in the Appendix.

Heavy metals were identified using both induction coupled (IC) plasma and atomic absorption spectroscopy. Two different digestion procedures, hot plate digestion and ampule digestion, were also evaluated prior to instrumental analysis.

Holzmacher, McLendon & Murrell, P.C.

Organic priority pollutants were analyzed using a Finnigan OWA-30 GC/MS/DS equipped with a Tekmar LSC-2 purge and trap sampler. EPA analytical methods 624 and 625, presented in the December 3, 1979, Federal Register(6), were used for the organics analyses. Pesticides and PCBs were initially analyzed by a Tracor model 550 gas chromatograph and confirmed by GC/MS only if the concentration of the compound was greater than 5 ug/l. Heavy metal priority pollutants were identified using a Perkin-Elmer 5000 atomic absorption spectrophotometer. Total cyanide analyses were performed according to method 335.2 in "Methods for Chemical Analysis of Water and Wastes," U.S. EPA, 1974.(7) Phenols were measured as a group by method 420.1 in "Methods for Chemical Analysis of Water and Wastes," U.S. EPA. March, 1979.(8) Quality control methods are cited in the Appendix.

Instrument Detection Limits

Table 6 presents the instrument detection limits for priority pollutant analyses performed by both H2M and the University of Washington. The higher detection limits reported by H2M for the volatile and extractable organic analyses of the treatment process effluents and wells after recharge were attributed to interferences from non-priority pollutants. The lower detection limits for pesticides/PCBs analyses of wells after discharge are attributable to lower concentrations of interfering

TABLE 6. INSTRUMENT DETECTION LIMITS (ug/l)

Priority Pollutants	Holzmacher, McLendon & Murrell, P.C. Reclamation AWT Processes	Recharge Wells Before Recharge	Recharge Wells After Recharge	Univ. of Washington Reclamation AWT Processes
Volatile Organics	10*	1	10*	0.05
Acid Extractables	25†	1	25†	0.05
Base/Neutral Extractables	10‡	1	10‡	0.05
Pesticides/PCBs				0.001
Aldrin	1	1	0.03	
a - BHC	1	1	0.03	
b - BHC	1	1	0.03	
d - BHC	1	1	0.03	
g - BHC	1	1	0.03	
P, P' - DDD	1	1	0.06	
P, P' - DDE	1	1	0.03	
P, P' - DDT	1	1	0.06	
Dieldrin	1	1	0.03	
Endosulfan I	1	1	0.03	
Endosulfan II	1	1	0.06	
Endrin	1	1	0.03	
Endrin aldehyde	1	1	0.08	
Heptachlor	1	1	0.04	
Heptachlor epoxide	1	1	0.03	
Chlordane	5	5	0.5	
Toxaphene	5	5	2.5	
Aroclor 1016	5	5	1.0	
Aroclor 1221	5	5	1.0	
Aroclor 1232	5	5	1.0	
Aroclor 1242	5	5	1.0	
Aroclor 1248	5	5	1.0	
Aroclor 1254	5	5	1.0	
Aroclor 1260	5	5	1.0	
Metals and Miscellaneous				
Antimony	200	200	200	2
Arsenic	2	2	2	1
Beryllium	20	20	20	0.1
Cadmium	1	1	1	NA
Chromium	20	20	20	NA
Copper	20	20	20	NA
Lead	2	2	2	NA
Mercury	0.5	0.5	0.5	0.5
Nickel	20	20	20	NA
Selenium	2	2	2	2
Silver	20	20	20	NA
Thallium	20	20	20	1
Zinc	20	20	20	NA
Total Cyanides	5	5	5	NA
Total Phenols	1	1	1	NA

* Acrolein, Acrylonitrile : 100 ug/l

† 2, 4 - Dinitrophenol, 2 - Methyl 4, 6 - Dinitrophenol : 60 ug/l
Pentachlorophenol : 80 ug/l ; 4 - Nitrophenol : 40 ug/l for 57% of samples, 60 ug/l for 43% of samples

‡ Indeno (1, 2, 3 - c, d) pyrene, Dibenzo (a, h) anthracene, Benzo (g, h, i) perylene : 25 ug/l

NA Not applicable

substances, permitting a greater degree of analytical resolution.

OVERALL PLANT PERFORMANCE RESULTS

During the initial phase of testing, a total of three plant effluent samples were collected from the chlorination storage reservoir, one each on April 6, May 19, and June 29, 1981. Raw wastewater samples were also collected from the influent channel to the grit tanks on each of the above-mentioned dates. These samples were analyzed to determine the constituents in the effluent prior to transmission to the recharge site and to evaluate the removal of priority pollutants across the AWT facility. Table 7 presents results of priority pollutants analyses for each of the six samples taken over this period plus the XAD concentrated effluent sample. The following sections describe these results as well as results obtained for non-priority pollutant analyses.

It should be noted that due to the limited number of samples analyzed, the data obtained are only indicative of the concentrations of the compounds detected. Percent removals for individual compounds are based on available data. If a compound was detected in the influent but not in the effluent, the detection limit was used as the effluent concentration value to compute the "% removal." Thus, a ">" preceeds such calculated removals, indicating minimum removal efficiencies.

Volatile Organics

A total of 18 of the 31 volatile organic priority pollutants were detected during the three sampling events. The concentrations of volatile organics were all below SPDES limitations, except during the second sampling event when tetrachloroethene was detected at a concentration of 11.2 ug/l.

On two sampling events, the trihalomethanes (THMs) bromodichloromethane, bromoform and dibromochloromethane were measured in the effluent, but were below detection limits in the influent. This indicates that these THMs may have been formed during chlorination. EPA's "Interim Report on the Fate of Priority Pollutants in POTWs" (EPA-440/1-80-301)(9) indicates 16 instances where the average concentration of bromodichloromethane increased, and 10 instances where the average dibromochloromethane concentration increased during chlorination, for the 20 POTWs studied.

The overall volatile organic removal efficiencies for the three sampling events are 80%, 80%, and 94%, with an average overall removal efficiency of 85%. Since it appears that THMs are produced across the plant, and since THMs were not detected

TABLE 7. OVERALL PRIORITY POLLUTANT REMOVALS AT THE CCWRP*

Compound	Collected 4/6/81 Influent	Effluent	% Removal	Collected 5/19/81 Influent	Effluent	% Removal	Collected 6/29/81 Influent	Effluent	% Removal	XAD Collected 4/6/81 Effluent
Volatile Organics										
Benzene	BDL	BDL		1.5	BDL	>97	6.5	BDL	>99	
Bromodichloromethane	BDL	2.7	(-)	BDL	3.4	(-)	BDL	BDL		
Bromoform	BDL	9.4	(-)	BDL	23.6	(-)	BDL	BDL		
Carbon tetrachloride	BDL	BDL		0.6	BDL	>92	0.5	BDL	>90	
Chlorobenzene	0.4	BDL	>88	BDL	BDL		0.1	BDL	>50	
Chloroform	6.8	1.3	81	11.5	1.3	89	13.9	3.9	72	
Dibromochloromethane	BDL	7.9	(-)	BDL	16.5	(-)	BDL	BDL		
Dichlorodifluoromethane	BDL	BDL		BDL	BDL		BDL	5.6	(-)	
1,1-Dichloroethane	2.4	BDL	>98	3.2	BDL	>98	3.0	BDL	>98	
1,2-Dichloroethane	BDL	BDL		BDL	BDL		2.4	BDL	>98	
Ethylbenzene	4.9	BDL	>99	1.7	0.2	88	3.4	0.6	82	
Methylene chloride	BDL	2.5	(-)	BDL	0.4	(-)	15.4	0.9	94	
Tetrachloroethene	38.1	4.1	89	39.7	11.2	72	BDL	BDL		
1,2-Trans-dichloroethene	BDL	BDL		BDL	BDL		8.0	BDL	>99	
1,1,1-Trichloroethane	18.9	0.1	>99	46.8	0.2	>99	24.4	BDL	>99	
Trichloroethene	47.0	0.9	98	104.3	1.2	99	BDL	BDL		
Toluene	26.8	0.7	97	118.0	1.1	99	31.0	1.2	96	
Vinyl chloride	BDL	BDL		0.1	BDL	>50	BDL	BDL		
TOTAL	145.3	29.6	80	327.4	64.7	80	108.6	6.6	94	
Base/Neutral Organics										
Acenaphthene	0.2	BDL	>76	BDL	BDL		BDL	BDL		BDL
Acenaphthylene	0.3	BDL	>81	BDL	BDL		0.4	BDL	>88	0.08
Anthracene	0.02	BDL		BDL	BDL		BDL	BDL		0.22
Bis (2-chloroethoxy) methane	4.5	BDL	>99	BDL	BDL		BDL	BDL		0.27
Bis (2-ethylhexyl) phthalate	117	40	66	39.1	10	74	347	125	64	1683
Butylbenzylphthalate	4.5	0.31	93	36.9	BDL	>99	BDL	BDL		2.2
2-Chloronaphthalene	0.06	BDL	>17	BDL	BDL		BDL	BDL		0.12
1,2-Dichlorobenzene	15.9	BDL	>99	86.7	BDL	>99	BDL	BDL		2.1
1,3-Dichlorobenzene	2.7	BDL	>98	10.7	BDL	>99	BDL	BDL		BDL
1,4-Dichlorobenzene	8.5	BDL	>99	71.6	BDL	>99	BDL	BDL		0.75
Diethyl phthalate	1.3	0.12	91	114	BDL	>99	11.9	BDL	>99	6.6
Dimethyl phthalate	1.4	BDL	>96	8.7	BDL	>99	BDL	BDL		1.3
Di-n-butyl phthalate	5.5	0.38	93	3.7	BDL	>99	49.1	3.4	98	5.6
2,6-Dinitrotoluene	0.7	BDL	>92	BDL	BDL		BDL	BDL		2.1
Di-n-octyl phthalate	BDL	BDL		BDL	BDL		29.1	BDL	>99	15.8
1,2-Diphenyl hydrazine	0.1	BDL	>50	2.5	BDL	>98	BDL	BDL		1.5
Fluoranthene	0.07	BDL	>29	1.3	BDL	>96	BDL	BDL		0.94
Fluorene	0.3	BDL	>83	0.4	BDL	>86	0.7	BDL	>93	0.54
Naphthalene	4.5	0.02	>99	2.4	BDL	>98	55.2	51.9	6	13.1
Nitrobenzene	0.8	BDL	>94	4.0	BDL	>99	BDL	BDL		1.1
N-nitrosodiphenylamine	0.8	BDL	>94	31.8	BDL	>99	BDL	BDL		BDL
Phenanthrene	0.6	BDL	>91	3.2	BDL	>98	2.2	BDL	>98	2.2
Pyrene	BDL	BDL		1.3	BDL	>95	BDL	BDL		0.70
TOTAL	169.75	40.83	76	418.3	10	98	495.6	180.3	64	1740.22
Acid Extractable Organics										
2,4-Dichlorophenol	BDL	BDL		3.0	BDL	>98	BDL	BDL		BDL
2,4-Dimethylphenol	0.02	BDL		1.6	BDL	>97	BDL	BDL		2.9
2-Nitrophenol	BDL	BDL		19.5	BDL	>99	BDL	BDL		BDL
Parachlorometacresol	1.8	BDL	>97	BDL	BDL		BDL	BDL		BDL
Phenol	0.4	BDL	>88	16.8	BDL	>99	35.7	BDL	>99	BDL
2,4,6-Trichlorophenol	0.2	BDL	>69	BDL	BDL		BDL	BDL		12.2
TOTAL	2.44	BDL	>98	40.9	BDL	>99	35.7	BDL	>99	15.1

TABLE 7. OVERALL PRIORITY POLLUTANT REMOVALS AT THE CCWRP* (Cont.)

Compound	Collected 4/6/81 Influent	Effluent	% Removal	Collected 5/19/81 Influent	Effluent	% Removal	Collected 6/29/81 Influent	Effluent	% Removal	XAD Collected 4/6/81 Effluent
Pesticides/PCBs										
Aldrin	BDL	BDL		320	4.4	99	BDL	BDL		BDL
Alpha-BHC	BDL	BDL		26.1	8.3	68	BDL	BDL		BDL
Alpha chlordane	BDL	BDL		BDL	BDL		2881	BDL	>99	BDL
Beta/gamma-BHC	BDL	88.7	(-)	95.8	12.1	87	EDL	BDL		BDL
Beta-endosulfan	59.3	34.4	42	47.5	45.4	4	714	BDL	>99	3.4
Delta-BHC	29.3	28.4	3	25.3	3.5	86	136	**	>50	5.9
Dieldrin	BDL	BDL		BDL	BDL		154	BDL	>99	BDL
Endosulfan sulfate	189	187	1	98.3	40.1	56	160	BDL	>99	6.9
Endrin	101	13.7	86	29.8	37.7	(-)	134	BDL	>99	6.4
Endrin aldehyde	127	112	12	351	116	67	270	BDL	>99	16.4
Heptachlor	40.4	33.4	17	322	7.7	98	BDL	BDL		3.7
Heptachlor epoxide	6.3	14.4	(-)	51.1	15.4	70	BDL	BDL		2.6
p,p'-DDD	BDL	140	(-)	BDL	BDL		1064	302	>72	BDL
p,p'-DDE	BDL	BDL		BDL	BDL		164	BDL	>99	BDL
p,p'-DDT	BDL	BDL		310	266	14	1538	370	>76	BDL
TOTAL	552.3	652.0	(-)	1676.9	556.6	67	7215	672	91	45.3
Metals†										
Arsenic (1)	3.6	2.6	28	2.0	BDL	>50	8.2	8.5	(-)	
Beryllium (2)	BDL	BDL		BDL	BDL		0.5	0.1	80	
Cadmium (2,3)	4.6	4.0	13	3.1	2.5	19	3.8	3.2	16	
Chromium (2)	19.8	9.4	53	9.5	1.7	82	12.3	0.8	93	
Copper (4,5)	149	24.9	83	125	3.0	98	137	19	86	
Lead (6)	6.4	0.6	91	8.9	0.9	90	9	0.8	91	
Nickel (5)	22.5	14.5	36	25	16	36	26	15	42	
Selenium (2)	BDL	BDL		BDL	BDL		4.4	2.0	55	
Silver (3)	37.8	2.7	93	7.2	0.1	99	11	3.8	66	
Zinc (2,3)	630	250	60	100	80	20	105	58	45	
TOTAL	873.7	308.7	65	280.7	104.2	63	317.2	111.2	65	

* = All concentrations in ug/l, except for the Pesticides/PCBs category and XAD Effluent, which are in ng/l.
Analyses performed at University of Washington.
BDL = Below detection limit (see Table 6).
** = Detected but not integrated.
(-) = Pollutant concentration is higher in the effluent than in the influent.
† = Metals were analyzed as follows:
(1) Hydride milled
(2) Ampule digestion with inductive coupled plasma
(3) Cadmium and Zinc on 5/19/81 analyzed by ampule digestion with graphite furnace
(4) Ampule digestion with graphite furnace
(5) Effluent Copper on 4/6/81 analyzed by ampule digestion with inductive coupled plasma
(6) Hotplate digestion with graphite furnace

in the effluent during the third sampling event, the 94% removal efficiency calculated for this event is more representative of an actual, rather than net, removal efficiency for volatile organics. Furthermore, by subtracting effluent THM concentrations for the first two events from their total volatile organic concentrations, removal efficiencies of 93% and 94% are obtained.

Extractable Organics

A total of 23 of the 47 base/neutral extractable organic priority pollutants were detected during the three sampling events. High concentrations of bis(2-ethylhexyl)phthalate, butylbenzylphthalate, di-n-butylphthalate, diethylphthalate, naphthalene, and 1,4- and 1,2-dichlorobenzene were detected in the raw wastewater. All base/neutral extractable organics were removed at efficiencies greater than 90% or to levels below detection, with the exception of bis(2-ethylhexyl)phthalate and naphthalene. These compounds were detected in the effluent at concentrations which exceeded SPDES limitations, during the third sampling event.

The overall removal efficiencies for the three sampling events were 76%, 98%, and 64%, resulting in an average overall percent removal of 79%. It should be noted, however, that one or two compounds dominate the calculations and that each average is based on a different number of monitored pollutants, with the 76% removal corresponding to the greatest number of compounds detected (20 out of 22).

A total of 6 of the 11 acid extractable organic priority pollutants were detected during the aforementioned sampling period. Individual compound removal efficiencies ranged from >69% to >99%. Overall removal efficiencies could not be determined because all effluent concentrations were below detection limits.

During the first testing period, XAD-2 resin was used to concentrate the organics present in the tertiary effluent. The results in Table 7 indicate that the resin was very effective in concentrating the organics, as most of the influent organics were also detected in the resin concentrate, albeit at 100 to 1000-fold lower concentrations.

Pesticides/PCBs

Chlorinated organic compounds - pesticides and polychlorinated biphenols (PCBs) - were detected using an electron capture equipped gas chromatograph. Since gas chromotographic identification is based on elution time and comparison with a standard, it is much less certain than the mass spectral identification used for the extractables. Detection limits are lower

than for other analytical methods, however, due to overlapping peaks and a shifting base line, quantitation is less reliable.

A total of 15 of the 25 chlorinated organics in the pesticides/PCBs priority pollutant category were detected during the three sampling events. The data presented in Table 7 indicate that, in some cases, effluent concentrations of these compounds were higher than influent concentrations. This is probably due to sampling and analytical anomalies rather than the formation of these compounds.

In general, removal efficiencies are highly dependent upon influent concentrations. A removal efficiency of 90% was achieved when the total influent pesticides/PCBs concentration was 7215 ng/l, 67% at an influent concentration of 1677 ng/l and essentially zero at 552 ng/l. Total effluent concentrations ranged from 550 to 675 ng/l which is apparently the lowest level achievable.

Metals

During the three sampling events, 10 of the 13 priority pollutant metals were detected using induction coupled plasma and/or atomic absorption spectroscopy. Two different digestion procedures were also employed in an attempt to achieve the most useful and accurate data. Table 8 presents a complete summary of metals analyses data. Results for the various analytical procedures including both priority and non-priority pollutant elements are shown.

Data presented in Table 7 depict the best data with respect to EPA protocol and detection limits. Individual metals removals ranged from 13% for cadmium to 99% for silver. Overall mass removals were consistent during the three sampling events with removal efficiencies of 65%, 63%, and 65%. Both influent and effluent concentrations of metals were well below SPDES limitations.

Non-Priority Trace Organics

Samples of the plant effluent were also analyzed for extractable and volatile non-priority organics. In the analyses for these non-priority pollutants, authentic standards were not used and corresponding response factors could not, therefore, be measured on a compound-by-compound basis, as was done for the priority pollutants.

The type of errors that typically arise in the GC/MS/DS analysis of these non-priority pollutants are incorrect compound identification and misleading concentrations. In order to avoid incorrect compound identification, non-priority organic compounds having "FIT" values of 900 or greater were selected

TABLE 8. HEAVY METALS IN RAW WASTEWATER AND CHLORINATED EFFLUENT AT THE CCWRP*

Element	Method	Collected 4/6/81 Influent	Effluent	% Removal	Collected 5/19/81 Influent	Effluent	% Removal	Collected 6/29/81 Influent	Effluent	% Removal
Antimony (Sb)	AD/GF	BDL	BDL		BDL	BDL		BDL	BDL	
Arsenic (As)	Hydr	3.6	2.6	28	2.0	BDL	>50	8.2	8.5	(-)
Barium (Ba)	AD/ICP				19	BDL	>95			
	HP/ICP				25	10	60			
Beryllium (Be)	AD/ICP	BDL	BDL		BDL	BDL		0.5	0.1	80
	HP/ICP				0.3	BDL	>66			
Cadmium (Cd)	AD/ICP	4.6	4.0	13				3.8	3.2	16
	AD/GF				3.1	2.5	19			
	HD/GF				3.3					
Chromium (Cr)	AD/ICP	19.8	9.4	53	9.5	1.7	82	12.3	0.8	93
	HD/ICP				9.7	2.1	78			
Cobalt (Co)	AD/ICP	8.1	5.8	28	BDL	BDL		4.1	1.7	58
	HD/ICP				1.0	0.8	20			
Copper (Cu)	AD/ICP	175	24.9	86		7.0		115	18	84
	HP/GF	135	12.4	91	121					
	AD/GF	149			125	3.0	98	137	19	86
	ND/GF	91	19	79						
	HP/ICP				96.5	12	88			
Iron (Fe)	AD/ICP	1630	65.4	96	1510	13.9	99	1340	20	99
	HP/GF	997	35.6	96						
	AD/GF	867	49	94	1500	50.9	97			
	ND/GF	712	22	97						
	HP/ICP				1510	66.3	96			
Lead (Pb)	HP/GF	6.4	0.6	91	8.9	0.9	90	9	0.8	91
	AD/GF	5.1	0.5	90	8	2	75			
	ND/GF	5.0	0.4	92						
Manganese (Mn)	AD/ICP	5670	134	98	165	32.1	81	135	26	86
	HP/ICP				163	34.6	79			
Mercury (Hg)	CV	BDL	BDL		BDL	BDL		BDL	BDL	
Nickel (Ni)	HP/GF	22.5	14.5	36	25	16	36	26	15	42
	AD/GF	35	10	71						
	ND/GF	30	10	67						
	AD/ICP				30	10	66			
Selenium (Se)	Hydr	BDL	BDL		BDL	BDL		4.4	2.0	55
Silver (Ag)	AD/ICP	37.8	2.7	93	7.2	0.1	99	11	3.8	66
	AD/GF				6.2	BDL	>84			
	HP/GF					0.16				
	ND/GF				10.4	0.3	97			
Thallium (Th)	ICP	BDL	BDL		BDL	BDL		BDL	BDL	
Zinc (Zn)	AD/ICP	630	250	60				105	58	45
	AD/GF				100	80	20			
	HP/ICP				92.8					
	HP/GF				90	83	8			

* Influent and effluent concentrations expressed as ug/l. Missing data indicates element not analyzed.

ICP = inductive coupled plasma
Hydr = hydride milled
CV = cold vapor
HP = hotplate digestion
AD = ampule digestion
ND = no digestion
GF = graphite furnace
(-) = effluent concentration greater than influent concentration
BDL = below detection limit

and presented in Table 9. "FIT" values represent a quantitative measure of the exactness of match between an experimental mass spectrum and a spectrum from the printed literature or a computer readable data base. On a scale of 1000, "FIT" values of 900 or more for any of the non-priority pollutants are believed to be representative of the "true" identities of the compounds. Concentrations of the organics shown in Table 9 are, however, approximate and provide only an order-of-magnitude estimate of their relative amounts.

During the second and third sampling periods, a total of 28 extractable organics were identified in the effluent. None of these organics were identified during the first sampling period. Two volatile organics were detected during the second sampling period and one pesticide was detected in the plant effluent during the third period.

Concentrations greater than 50 ug/l were identified in the effluent for 1,3,5,7-cyclooctatetraene; 4-hydroxy-4-methyl-2-pentanone; 5-triazolo(4,3-b)pyridazine-6-ol; 1,1,3-trimethylcyclopentane; trimethyl octane; 3,5,24-trimethyl tetracontane; and 4-fluorobenzenamine. The concentrations of volatile organics were much lower than those of the extractable organics, as was the pesticide.

Overall Plant Performance Summary

This initial investigation identified the constituents present in the effluent to be used for groundwater recharge and evaluated the overall removal of priority pollutants by the treatment plant.

Seventy-two (72) priority pollutants were identified in the raw wastewater and/or the plant effluent including: 18 volatile, 23 base/neutral extractable and 6 acid extractable organics; 15 chlorinated hydrocarbons; and 10 heavy metals. Thirty-five (35) non-priority pollutants were also identified including: 2 volatile organics, 28 extractable organics, one pesticide and 4 heavy metals.

Some of the volatile compounds, such as tribromomethane, dibromochloromethane, bromodichloromethane, and dichlorofluoromethane appear to be generated in the plant as a result of chlorination. This potential effect of chlorination was investigated further in Phase II testing and will be discussed later.

Since the effluent concentrations of most of the organics were below the detection limits of the direct extraction procedure, XAD-2 resin was used to concentrate the effluent organics present in concentrations below 0.1 ppb, as a means of estimating their removals by the treatment system. Comparison of influent

TABLE 9. NON-PRIORITY POLLUTANT ORGANICS IN CHLORINATED EFFLUENT AT THE CCWRP*

Compounds**	Collected 4/6/81 Effluent	Collected 5/19/81 Effluent	Collected 6/29/81 Effluent
1 - Azabicyclo (3, 1, 0) hexane	BDL	13.8	BDL
Benzaldehyde	BDL	BDL	38.0
Bischloroethylether	0.2	BDL	BDL
Bromoethene	BDL	5.3	BDL
1 - Cyclobutylethanone	BDL	BDL	20.5
1, 3, 5 - Cycloheptatriene	BDL	BDL	26.5
2 - Cyclohexen - 1 - ol	BDL	26.6	BDL
1, 3, 5, 7 - Cyclooctatetraene	BDL	BDL	500
2, 3 - Dimethylcyclobutanone	BDL	BDL	5.3
3, 3 - Dimethylhexane	BDL	29.4	BDL
5 - Ethyl - 2 - methylheptane	BDL	BDL	27.1
4 - Fluorobenzenamine	BDL	BDL	50.3
4 - Hydroxy - 4 - methyl - 2 - pentanone	BDL	BDL	113.3
1H - tetrazol - 5 - amine	BDL	11.0	BDL
Isooctanol	BDL	BDL	18.9
1 - Methylaziridine	BDL	7.6	BDL
2 - Methylaziridine	BDL	18.7	BDL
1 - Methylethylbenzene	BDL	BDL	44.4
1 - Methyl - 1h - pyrrole	BDL	19.8	BDL
7 - Methylnonanoicacid, methylester	BDL	5.1	BDL
4 - Methyl - 2 - propyl - 1 - pentanol	BDL	26.0	BDL
3 - Pentanone	BDL	8.1	BDL
S - Triazolo (4, 3 - b) pyridazin - 6 - ol	BDL	81.6	BDL
Trifluoromethane	BDL	BDL	4.0
1, 1, 3 - Trimethylcyclopentane	BDL	80.8	BDL
3, 5, 5 - Trimethyl - 1 - hexene	BDL	29.6	BDL
Trimethyloctane	BDL	59.5	BDL
3, 5, 24 - Trimethyltetracontane	BDL	54.4	BDL
Dibromomethane†	BDL	1.1	BDL
Tetrafluoromethane†	BDL	0.4	BDL
Mirex‡	BDL	BDL	1.6

* Values expressed in ug/l
** Compounds having "FIT" value $\geq$ 900
† Volatile Organics
‡ Chlorinated Organic
BDL Below Detection Limit of 0.05 ug/l

and effluent concentrations indicated a greater than 90% removal for most constituents, reflecting the effectiveness of the unit processes.

PERFORMANCE RESULTS OF INDIVIDUAL UNIT PROCESSES

A total of 23 samples were collected to evaluate the effectiveness of individual treatment processes - chemically aided primary clarification, biological treatment, filtration and carbon adsorption - for the removal of priority pollutants, and to evaluate the affect of chlorination on plant effluent characteristics. Tables 10a and 10b present the results of sample analyses for only those compounds detected at each sampling location. It should be noted that no pesticides, PCBs or acid extractable priority pollutants were detected in any sample during this phase of the testing program.

Chemically Aided Primary Clarification

Three samples were collected at the effluent channel from the grit removal facilities; one each on September 28, October 14 and October 24, 1982. Samples were also taken from the primary effluent on the above-mentioned dates. The analytical results for these six samples are presented in Table 10a.

During the three sampling events, a total of 13 out of 31 volatile organics were detected in the primary influent, 9 of which were present at concentrations above the quantification limit of 10 ug/l. Eight volatile organics were detected in the primary effluent, five of which were above the quantification limit. Based on total volatile organics mass, removals for the three samples were approximately 68%, 38% and 8%, with an average value of 38%.

A total of 4 out of 47 base/neutral extractables were detected in the primary influent only during one sampling event. A total of 3 extractables were detected in the primary effluent during another sampling event. The base/neutral extractables detected were all below the quantification limit of 10 ug/l; thus, no conclusions regarding removal efficiencies can be drawn.

A total of 8 out of 13 priority pollutant metals were detected in the primary influent and effluent during the three sampling events. Based on total mass, removals for the first and second sampling events were approximately 29% and 76%, respectively.

The calculated percent removal for the third sampling event resulted in a negative value, primarily due to a high copper concentration in the effluent.

TABLE 10a. EFFECT OF INDIVIDUAL UNIT PROCESSES ON PRIORITY POLLUTANT CONCENTRATIONS AT THE CCWRP (ug/l)

	Primary Treatment									Biological Treatment								
	Collected 9/28/82			Collected 10/14/82			Collected 10/29/82			Collected 10/5/82			Collected 10/15/82			Collected 10/29/82		
Compound	Pri. Inf.	Pri. Eff.	% Rem.	Pri. Inf.	Pri. Eff.	% Rem.	Pri. Inf.	Pri. Eff.	% Rem.	Pri. Eff.	FT#7 Eff.	% Rem.	Pri. Eff.	FT#7 Eff.	% Rem.	Pri. Eff.	FT#7 Eff.	% Rem.
Volatile Organics																		
Bromoform	30	BDL	>67	98	BDL	>90	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Chlorobenzene	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Chloroform	11	*	>9	*	*		*	*		*	BDL		*	BDL		*	BDL	
Cis/Trans-1,2-Dichloroethene	*	BDL		BDL	*		*	*		BDL	BDL		*	BDL		*	BDL	
Dibromochloromethane	11	BDL	>9	16	BDL	>38	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
1,2-Dichloroethane	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Ethylbenzene	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Methylene chloride	14	11	21	*	18	(-)	26	13	50	10	BDL		34	BDL	>71	13	BDL	>22
Tetrachloroethene	18	12	33	*	17	(-)	47	72	(-)	10	BDL		22	BDL	>55	72	BDL	>86
Toluene	*	11	(-)	*	21	(-)	12	*	>17	9	BDL		23	BDL	>57	*	BDL	
1,1,1-Trichloroethane	25	13	48	17	26	(-)	22	11	50	15	BDL	>33	30	BDL	>67	11	BDL	>9
Trichloroethene	14	*	>29	*	*		15	16	(-)	*	BDL		*	BDL		16	BDL	>38
Trichlorofluoromethane	26	*	>62	*	*		BDL	BDL		BDL	BDL		*	BDL		BDL	BDL	
Base/Neutral Extractables																		
Bis (2-ethylhexyl) phthalate	BDL	BDL		BDL	BDL		BDL	BDL		180	BDL	>94	BDL	BDL		BDL	BDL	
Butyl benzyl phthalate	BDL	BDL		BDL	*		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
1,2-Dichlorobenzene	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
1,3-Dichlorobenzene	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
1,4-Dichlorobenzene	*	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Diethyl phthalate	*	BDL		BDL	*		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Naphthalene	BDL	BDL		BDL	*		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Di-n-butyl phthalate	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		BDL	BDL	
Metals and Miscellaneous																		
Arsenic	BDL	BDL		BDL	BDL		BDL	6	(-)	BDL	BDL		BDL	BDL		6	BDL	>67
Cadmium	BDL	BDL		1.2	BDL	>17	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Chromium	BDL	BDL		30	20	33	BDL	30	(-)	BDL	BDL		BDL	BDL		30	BDL	>33
Copper	90	80	11	290	60	79	100	250	(-)	80	20	75	60	20	67	250	BDL	>92
Lead	BDL	BDL		31	7	77	15	9.5	37	11	5	55	8	BDL	>75	9.5	6	37
Mercury	BDL	BDL		0.85	BDL	>41	0.65	BDL	23	BDL	BDL		BDL	BDL		BDL	BDL	
Nickel	160	80	50	BDL	BDL		20	BDL		BDL	BDL		BDL	20		BDL	BDL	
Zinc	90	80	11	220	50	77	190	80	58	80	BDL	>75	50	BDL	>60	80	20	75
Total Cyanides	20	20	0	10	BDL	>50	10	20	(-)	BDL	BDL		BDL	BDL		20	10	50
Total Phenols	14	22	(-)	8	72	(-)	14	44	(-)	26	11	58	18	BDL	>94	44	BDL	>98

BDL: Below Detection Limit

* : Detected, but less than a quantification limit of 10 ug/l

(-): Pollutant concentration in the effluent is higher than in the influent

TABLE 10b. EFFECT OF INDIVIDUAL UNIT PROCESSES ON PRIORITY POLLUTANT CONCENTRATIONS AT THE CCWRP (ug/l)

	Filtration/Carbon Adsorption									Chlorination								
	Collected 10/8/82			Collected 10/26/82			Collected 10/27/82			Collected 8/19/82			Collected 9/11/82			Collected 10/13/82		
	FT#7	Ads.	%	FT#7	Ads.	%	FT#7	Ads.	%	Ads.	Chlor.	%	Ads.	Chlor.	%	Ads.	Chlor.	%
Compound	Eff.	Eff.	Rem.	Eff.	Eff.	Rem.	Eff.	Eff.	Rem.	Eff.	Eff.	Chg.	Eff.	Eff.	Chg.	Eff.	Eff.	Chg.
Volatile Organics																		
Benzene	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		*	BDL	
Bromodichloromethane	BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		BDL	BDL		BDL	*	
Bromoform	BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		BDL	45	(-)	BDL	220	(-)
Chloroform	BDL	BDL		BDL	BDL		BDL	BDL		*	BDL		*	*		BDL	*	
Dibromochloromethane	BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		BDL	57	(-)	BDL	37	(-)
Methyl chloride	BDL	BDL		BDL	BDL		BDL	BDL		*	*		*	BDL		BDL	*	
Tetrachloroethene	BDL	BDL		BDL	*		BDL	BDL		*	*		*	*		*	*	
Toluene	BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		BDL	BDL		BDL	BDL	
1,1,1-Trichloroethane	BDL	BDL		BDL	BDL		BDL	BDL		BDL	*		*	*		37	*	>73
1,1,2-Trichloroethane	BDL	BDL		BDL	BDL		BDL	BDL		*	BDL		BDL	*		BDL	BDL	
Trichlorofluoromethane	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		*	BDL		BDL	*	
Base/Neutral Extractables																		
Bis (2-ethylhexyl) phthalate	BDL	230	(-)	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	
Metals and Miscellaneous																		
Copper	BDL	20		20	20	0	BDL	BDL		BDL	BDL		30	30	0	30	BDL	>33
Lead	5	BDL	>60	BDL	BDL		BDL	BDL		BDL	BDL		BDL	3	(-)	BDL	BDL	
Mercury	BDL	BDL		BDL	BDL		BDL	BDL		BDL	0.7	(-)	BDL	BDL		BDL	BDL	
Nickel	20	BDL		BDL	BDL		BDL	BDL		BDL	30	(-)	BDL	BDL		40	BDL	>50
Silver	BDL	30	(-)	BDL	BDL		BDL	BDL		BDL	BDL		30	BDL	>67	BDL	BDL	
Zinc	20	20	0	20	20	0	20	20	0	20	30	(-)	30	30	0	BDL	20	(-)
Total Cyanide	20	20	0	BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL		BDL	BDL	

BDL: Below Detection Limit

* : Detected, but less than a quantification limit of 10 ug/l

(-): Pollutant concentration in the effluent is higher than in the influent

The levels of total phenols increased after primary clarification for all three sampling events. Total cyanide increased, decreased and remained the same across the primary treatment system for the three events. It appears that primary treatment is not effective in removing these compounds. Furthermore, phenols present in influent suspended solids could be solubilized under the increased pH of the primary treatment system.

Biological Treatment

Biological treatment consists of carbon oxidation-nitrification, denitrification and post aeration processes. In order to evaluate the biological treatment system for the removal of priority pollutants, samples were collected from the Primary Sedimentation Tank and Final Tank No. 7 effluent flows on October 5, October 15 and October 29, 1982. The results of laboratory analyses for these samples are shown in Table 10a.

A total of 8 volatile organics were detected in the primary effluent during the three sampling events. After the combined carbon oxidation-nitrification and dentrification processes, the concentrations of all volatile organics were at levels below the detection limit.

Of the base/neutral extractable organics, only bis(2-ethylhexyl)phthalate was detected in the primary effluent. This compound, however, was not detected in the Final Tank No. 7 effluent. Using the detection limit as the effluent value, a removal efficiency of >94% was calculated.

A total of 5 priority pollutant metals were detected in the primary effluent and 3 metals were detected in the Final Tank No. 7 effluent during the three sampling events. Based on the total mass of the detected metals, removals for the three samples were 68%, 87% and 93%, with an average value of 81%.

The concentrations of total phenols were reduced to levels below detection during the second and third sampling events. For the first sampling event, total phenol removal efficiency was 58% with an effluent concentration of 11 ug/l. An average phenol removal efficiency of greater than 83% for the three events suggests good removal of phenol through biological treatment.

Cyanide was detected only during the third sampling event. At this time, the total cyanide concentration was reduced by 50% across the biological treatment system. Other priority pollutants, such as the acid extractables and pesticides/PCBs, were all below detection levels.

Filtration/Carbon Adsorption

In order to evaluate the filtration/carbon adsorption processes for the removal of priority pollutants, three samples were collected at the effluent from Final Tank No. 7; one each on October 8, 26 and 27, 1982. Samples were also collected from the carbon adsorber effluent on the above-mentioned dates. These samples were analyzed and the results are presented in Table 10b.

The concentrations of volatile organics in Final Tank No. 7 effluent and carbon adsorber effluent were all below the detection limit, except for tetrachloroethene, which was detected in the adsorber effluent but was below the quantification limit.

The concentrations of base/neutral extractables in Final Tank No. 7 effluent and carbon adsorber effluent were all below the detection limit, except for bis(2-ethylhexyl)phthalate. The relatively high level of this phthalate compound was found in only one carbon adsorber effluent sample and, thus, could be due to sample contamination or analytical error.

The removal of metals by filtration/carbon adsorption is difficult to evaluate since the majority of metals concentrations were below detection levels.

Unit Process Performance Summary

It is difficult to draw firm conclusions regarding unit process performance for the removals of priority pollutants due to the small sample size, three sampling events per process, and the fact that many compounds were below detection levels. In a few cases, pollutant concentrations in the effluent were found to be higher than their corresponding concentrations in the influent, resulting in a large variation in average removal efficiencies. Nevertheless, the data in Tables 10a and 10b indicate that biological treatment is the major removal process for volatile organics. However, air stripping during post aeration, rather than biodegradation, may be the major removal mechanism.

Chemically aided primary clarification and biological treatment are almost equally important for the removal of metals. It should be noted that metals removal across the biological treatment system may be enhanced by the alum and polymer addition prior to final sedimentation. Based on the total pollutant mass at each sampling location over the three sampling events, volatile organics were removed through primary clarification by 41% and further removed through biological treatment to below detection levels. Heavy metals were removed through

biological treatment to 93%. Further metals removal by filtration/carbon adsorption appears to be negligible from the available data.

EFFECT OF CHLORINATION

Samples were collected from the carbon adsorption unit effluent and the plant effluent on August 19, September 11 and October 13, 1982. The plant effluent was sampled at the chlorine contact tank discharge. Sample analyses were performed to evaluate the effect of chlorination. The results of these analyses are presented in Table 10b.

A total of 6 volatile organics were detected in the adsorber effluent during the three sampling events. After chlorination, however, a total of 10 volatile organics were detected in the chlorinated effluent. It appears that several volatile organics - most notably, trihalomethanes (THMs) - were formed during chlorination. These compounds were, in order of decreasing concentration: bromoform, dibromochloromethane, chloroform and bromodichloromethane.

The concentrations of bromoform and dibromochloromethane were, in some cases, higher than their maximum discharge concentrations of 50 ug/l, as stipulated in the facility's SPDES permit. Furthermore, the total trihalomethane (TTHM) concentrations for the second and third sampling events were 102 and 257 ug/l, respectively. These values are higher than the maximum contaminant level of 100 ug/l specified in the U. S. EPA's drinking water standards, promulgated November 29, 1979.(10)

The formation of THMs is reported in the literature to be a result of a complicated interaction of aqueous halogen species with natural aquatic humic substances, i.e., humic and fulvic acids. In general, several factors affect the formation of THMs including chlorine dose and type, detention time, pH, characteristics and concentrations of precursors, and bromide and iodide concentrations.

Figure 3 depicts the relationships between THMs, COD, chlorine dose, residual chlorine and pH. Data were obtained from CCWRP operating data for the 19 month period from April 1981 through October 1982.(11) The concentration of COD as an indicator of precursor presence in the water appears to correlate with THM concentrations.

In July 1982, the chlorine dose was increased from 3 to 4 mg/l due to more stringent requirements imposed upon coliform bacteria counts in the plant effluent. Generally, TTHM concentrations were higher after this operational change. Furthermore,

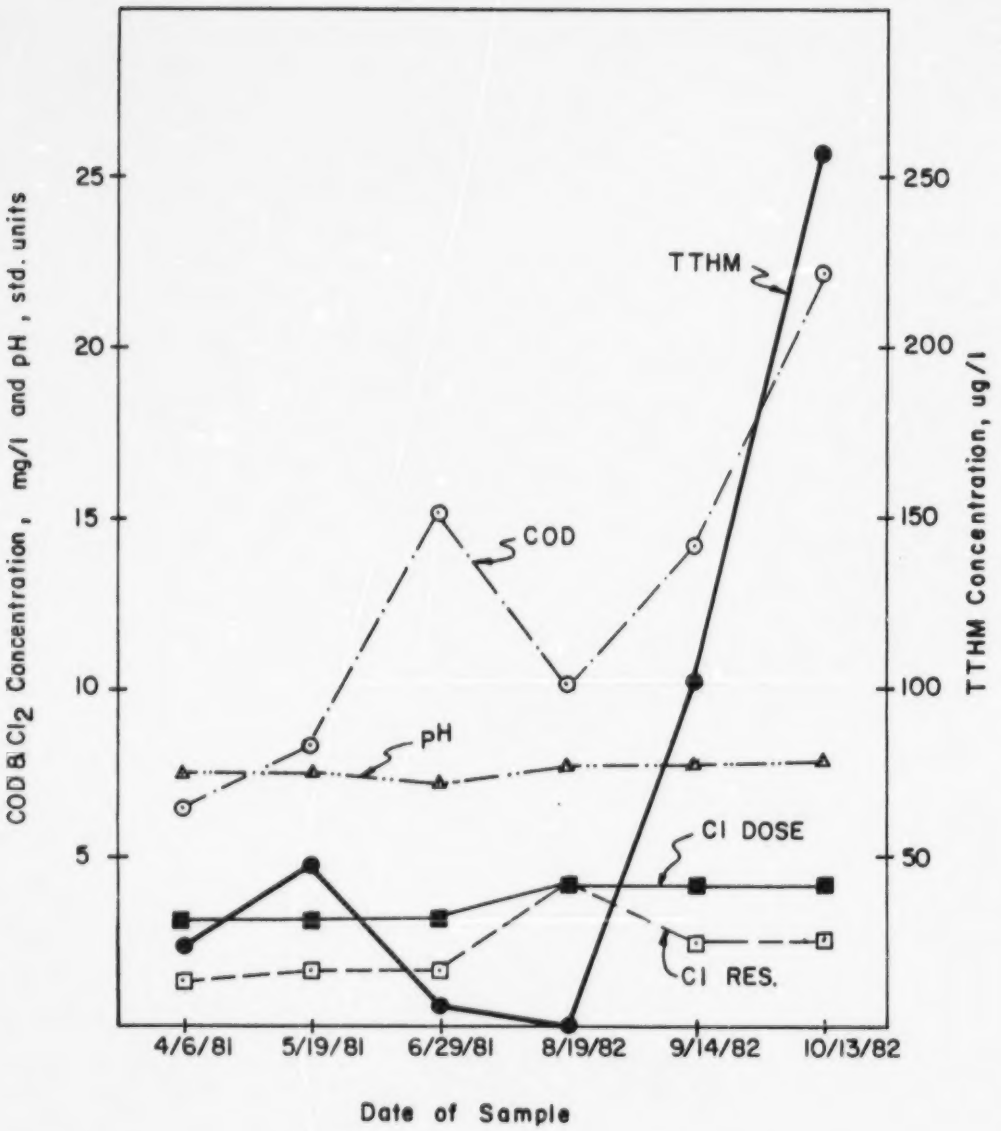

Figure 3. Relationship between chlorine dose, residual chlorine, COD, pH and THMs.

on October 13, 1982, an extremely high TTHM level was measured along with a high COD concentration at the higher chlorine dose.

The effluent pH values were relatively constant over the seven month period investigated; thus, no conclusions could be drawn with respect to THM formation. The effect of reaction time will be discussed later as it relates to the effect of recharge on groundwater quality.

In order to reduce the concentrations of THMs in the plant effluent, the following options were considered:

1) reduction of chlorine dose while maintaining acceptable bacteriological quality,

2) use of alternate disinfectants such as chlorine dioxide or ozone,

3) identification of specific organic precursors, and

4) improved efficiency of the carbon adsorption system, through more frequent regeneration or increased contact time, to reduce the concentration of precursors.

Recharge operations at Cedar Creek were suspended as the levels of THMs exceeded SPDES permit limitations and could not be reduced immediately. Due to the constraints of the chemical feed equipment, alternate disinfectants could not be utilized; however, the plant staff was able to reduce the chlorine residual from 2.5 mg/l to 1.5 mg/l. Also, the detention time of the carbon adsorption process was increased by operating two adsorbers in parallel for the recharge flow of 0.088 m^3/s. (Note: This recharge flow is half of the design flow since deep well recharge was not being utilized at the time.) Although these operational changes resulted in the reduction of THMs to levels within the permit's limits, this reduction was short lived as it became apparent that the activated carbon in the three adsorbers which were available for use was exhausted and had to be regenerated.

Due to the failure of the underdrain system of the fourth adsorber at the AWT plant, the regenerated carbon in the regenerated carbon storage tank could not be moved to this unit, and for this reason, the exhausted carbon in the three adsorbers could not be regenerated (i.e., there was no place to store the regenerated carbon until the fourth adsorber was placed back into service).

In light of the above, groundwater recharge operations were suspended until the fourth adsorber is repaired and the carbon in the other three adsorbers is regenerated as a potential means of reducing the concentration of organic precursors to levels low enough to prevent the formation of THMs.

SECTION 7

PRIORITY POLLUTANTS AT THE GROUNDWATER RECHARGE SITE

In order to determine the baseline concentrations of priority pollutants in the aquifer below the recharge site, samples were collected at each of the six monitoring wells on May 11, 1982, prior to commencement of recharge operations. Recharge operations began on October 6, 1982 with 0.088 m^3/s (2.0 mgd) of recharge water divided equally between Basins 1, 5, 6 and 7. On October 29, 1982, two well samples (11C and 12B) were collected. The other four well samples were not collected at the time this report was prepared because the recharge wastewater had not yet reached the monitoring wells, according to conductivity tests performed by the U. S. Geological Survey.(12) The analytical results for the eight samples are presented in Table 11.

Bis(2-ethylhexyl)phthalate was found in two well samples before recharge. All other base/neutral extractables were below the detection limit. All acid extractable organics were also below the detection limit. Copper and zinc were frequently detected in the monitoring wells before recharge. However, after recharge, the concentrations of all priority pollutant metals were at levels below detection.

A total of 7 volatile organics were detected in the monitoring wells before recharge. Most of these organics were found in a majority of the monitoring wells, indicating previous contamination of the aquifer. The volatiles having high concentrations include, in order of decreasing magnitude, tetrachloroethene, cis/trans-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene and 1,1-dichloroethane.

A recent study by the Nassau-Suffolk Regional Planning Board (1978)(13) demonstrated the widespread presence of low-molecular-weight halogenated hydrocarbons in the groundwater beneath Long Island. Trichloroethene, chloroform, 1,1,1-trichloroethane and tetrachloroethene were all observed at concentrations greater than 50 ug/l in the Upper Glacial and Magothy Aquifers.

This agrees with findings presented herein and those of Katz and Mallard (1981)(14) for the recharge area. Table 12 shows

TABLE 11. EFFECT OF RECHARGE ON PRIORITY POLLUTANT CONCENTRATIONS IN MONITORING WELLS AT THE CEDAR CREEK RECHARGE FACILITIES (ug/l)

Compound	Well 4B			Well D6			Well 11B			Well 11C			Well 12A			Well 12B		
	Before Rech.	After Rech.	% Chg.	Before Rech.	After Rech.	% Chg.	Before Rech.	After Rech.	% Chg.	Before Rech.	After Rech.	% Chg.	Before Rech.	After Rech.	% Chg.	Before Rech.	After Rech.	% Chg.
Volatile Organics																		
Bromodichloromethane	BDL			BDL			BDL			BDL	34	(-)	BDL			BDL	33	(-)
Bromoform	BDL			BDL			BDL			BDL	124	(-)	BDL			BDL	110	(-)
Chloroform	BDL			BDL			BDL			BDL	*		BDL			BDL	*	
Cis/Trans-1,2-dichloroethene	*			230			BDL			BDL	BDL		6			BDL	BDL	
Dibromochloromethane	BDL			BDL			BDL			BDL	98	(-)	BDL			BDL	115	(-)
1,1 Dichloroethane	6			BDL			43			19	BDL	>47	34			*	BDL	
1,1 Dichloroethene	BDL			*			10			*	BDL		8			BDL	BDL	
Methylene Chloride	BDL			BDL			BDL			BDL	BDL		BDL			BDL	*	
Tetrachloroethene	20			600			8			*	BDL		*			BDL	*	
1,1,1-Trichloroethane	9			*			49			50	BDL	>80	46			5	*	
Trichloroethene	*			55			*			BDL	BDL		55			*	BDL	
Trichlorofluoromethane	*			*			BDL			*	BDL		*			*	BDL	
Base/Neutral Extractables																		
Bis (2-ethylhexyl) phthalate	63			33			BDL			BDL	BDL		BDL			BDL	BDL	
Metals																		
Copper	20			BDL			80			30	BDL	>33	BDL			BDL	BDL	
Lead	3			BDL			BDL			BDL	BDL		BDL			BDL	BDL	
Zinc	20			BDL			BDL			70	BDL	>71	20			BDL	BDL	

BDL: Below detection limit

* : Detected, but less than a quantification limit of 10 ug/l

(-): Pollutant concentration in the wells is higher after recharge than before recharge.

TABLE 12. PRIORITY POLLUTANTS DETECTED IN WATER FROM OBSERVATION WELLS ON OR SURROUNDING THE RECHARGE SITE*

Compound(s)	Detection Limit (ug/l)	Depth of Well Screen Below Land Surface (feet)	Number of Wells Sampled	Number of Wells Detected	Maximum Concentration (ug/l)
Trichloroethene	20	50	21	3	173
		100	15	5	270
		200	9	1	290
Tetrachloroethene	20	50	21	5	580
		100	15	5	1500
		200	9	2	1000
Chloroform	20	50	21	1	21
		100	15	1	20
		200	9	0	--
1,1,1 - Trichloroethane	20	50	21	14	208
		100	15	4	87
		200	9	0	16
Dieldrin	0.01	50	21	17	0.22
		100	15	8	1.4
		200	9	2	0.08
Heptachlor epoxide	0.01	50	21	3	0.03
		100	15	1	0.01
		200	9	1	0.02
PCBs	0.1	50	21	7	0.6
		100	15	2	0.6
		200	9	0	--

*Source: Katz, B.G. and Mallard, G.E., "Chemical and Microbiological Monitoring of a Sole-Source Aquifer Intended for Recharge, Nassau County, New York," 1981.

that, in the recharge area, at least one of these four compounds was detected in water from most wells and from both aquifers.

Furthermore, concentrations of trichloroethene and tetrachloroethene increase with depth below land surface; the highest percentage of samples that exceeded 20 ug/l was in the 100-foot level. In contrast, both the maximum concentration of 1,1,1-trichloroethane and the percentage of samples exceeding 20 ug/l of this compound decrease with increasing depth. In addition, pesticides and PCBs have been detected in the groundwater. PCBs were detected in the two upper zones, while dieldrin and heptachlor epoxide were found in all three zones. For the three compounds, as the depth below land surface increases, the number of wells containing detectable concentrations decreases.

While not detected in any of the monitoring wells before recharge, THMs were detected at significant levels after recharge. TTHM concentrations for the two well samples (11C, and 12B) after recharge were 256 and 258 ug/l, respectively. These levels are higher than the maximum contaminant level of 100 ug/l specified in EPA's promulgated drinking water standards of 1979. They are also at or above levels measured in the CCWRP effluent.

As discussed previously, several factors affect the formation of THMs. Figure 4 demonstrates the effect of detention time on THM formation. The average concentration of TTHM in the chlorine contact tank was 72 ug/l (Point A), based on the analyses of six samples ranging from 0 to 257 ug/l. At a recharge flow rate of 0.11 m^3/s (2.5 mgd), the chlorinated effluent storage tank at the CCWRP and the 10.1 km transmission line provide detention times of 15 and 8 hours, respectively. Based on three samples obtained from the CCWRP's monthly lab reports(11), the concentrations of TTHM in the reservoir at the recharge site ranged from 13.3 to 146 ug/l, with an average value of 92 ug/l (Point B).

The U.S.G.S. estimated that the recharged water takes approximately 16 days to reach well 11C and 25 days to reach well 12B from the nearest respective recharge basin. This corresponds to lateral velocities of 1.14 m/d towards well 11C and 0.73 m/d towards well 12B. The TTHM concentrations were 256 ug/l for well 11C (Point C) and 258 ug/l for well 12B (Point D) based on analyses of the two samples collected on October 29, 1982.

This analysis indicates that as detention time increases, the formation of THMs increases. It also appears that the formation of THMs levels off for longer detention times, i.e. greater than 15 days, as shown by the similar TTHM concentrations at wells 11C and 12B. However, this latter result could

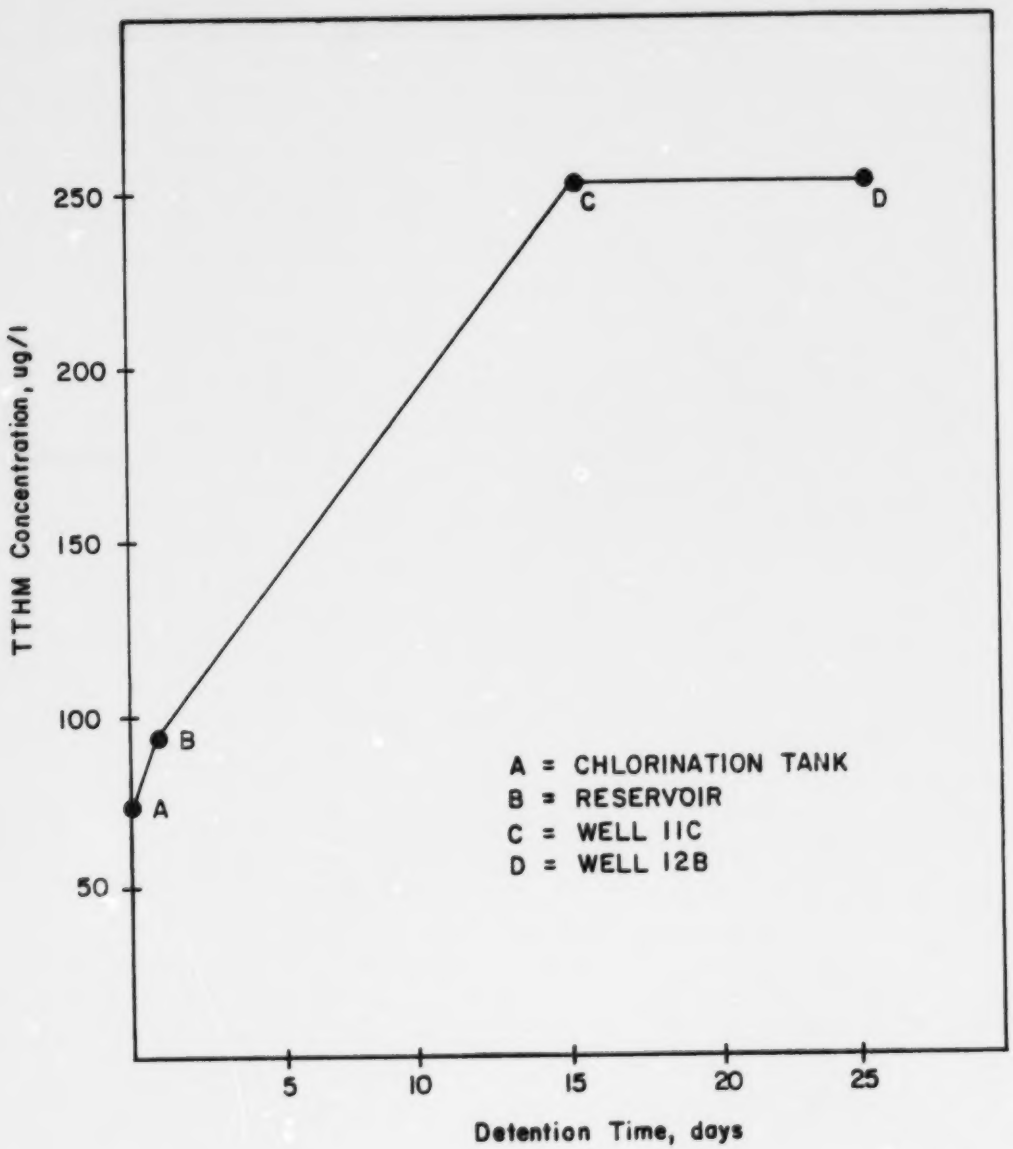

Figure 4. Effect of detention time on THM formation.

be due to the fact that the water mass was different for the two samples.

As stated previously, residual chlorine levels may be associated with THM formation. An investigation of plant operating data indicates that, with a chorine dose of 4 mg/l, the residual chlorine concentration after 15 minutes contact time ranged from 2.0 to 2.8 mg/l, with an average of 2.4 mg/l. The level of residual chlorine in the recharge site reservoir ranged from 0.2 to 1.2 mg/l, with an average of 0.47 mg/l. This analysis implies that as the detention time increases, the residual chlorine concentration decreases and THMs are formed. Furthermore, the level of residual chlorine in the recharge water may account for additional THM formation in the aquifer albeit at a lower rate than occurs in the transmission line where chlorine levels are higher.

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APPENDIX

QUALITY CONTROL METHODS USED BY SUBCONTRACTORS FOR PRIORITY POLLUTANT ANALYSES

H2M LABORATORY
ENVIRONMENTAL and INDUSTRIAL ANALYTICAL SERVICES

October 3, 1983

Mr. Thomas Brisbin
Consoer Townsend Associates
303 East Wacker Drive
Chicago, Illinois 60601

Dear Mr. Brisbin:

Enclosed please find a copy of our Quality Control Methods used during the analysis of "priority pollutant" samples, in conjunction with the "Cedar Creek Wastewater Reclamation Facility".

We trust this meets your needs. Should you have any questions or comments, please contact me at (516) 694-3040 anytime.

Very truly yours,

H2M LABORATORY

Stanley C. Lewis

SCL:vm

575 BROAD HOLLOW ROAD, MELVILLE, N.Y. 11747 • 516-694-3040

1.0 - QUALITY CONTROL PROTOCOL AND QUALITY ASSURANCE FOR ANALYSIS OF PRIORITY POLLUTANT PESTICIDES BY GC/ECD

1.1 - Summary of Analytical Method

The sample preparation and analysis follows the EPA Method 625 for analysis of priority pollutants in the Federal Register, Volume 44, No. 233 (December 3, 1979).

The concentrated extract from the basic extraction (or the combined extracts for phenols and base neutrals) is solvent exchanged, i.e., the methylene chloride is replaced with hexane.

Analysis is performed on a gas chromatograph with electron capture detector.

1.2 - Method Validation (QC)

1.2.1 - Calibration of Detector Response

The standing current for the electron capture linearizer is adjusted to optimize linearity. The response curve is developed with four pesticide solutions of concentrations ranging from 50 pg to 50 ng. Once linear response over the entire range is established, response factors for external standard method for all components are established by a "one point calibration", repeating injections of the same concentration.

Accuracy of the calibration is validated by analysis of "known" solutions from the EMSL Division of EPA, and comparing the results with the known values. The calibration is acceptable if the deviation of the calculated and known value is less than 20% of the known concentration.

1.2.2 - Evaluation of Sample Preparation Technique

1.2.2.1 - Recovery

Clean water is spiked with 3 ml of a standard solution in methanol, and subject to the sample preparation and analytical procedure. The results are evaluated for the recovery of the individual components.

1.2.2.2 - Precision

The recovery data for each component from these matrix spike analyses are compiled and evaluated for precision. The data for the standard deviation over a longer monitoring period (recovery data for 1981 and 1982 were combined) are used as guidelines for acceptability of routinely run spiked clean water samples.

1.3 - Routine Monitoring of Method Performance (QA)

1.3.1 - Stability in Calibration of Gas Chromatograph

Standard mixes containing all chlorinated pesticides to be analyzed are run each day when pesticides are analyzed. The daily response factors are recorded. Factors are considered acceptable if they remain within 2 x standard deviation of the average of the previous factors. Changes above the normal deviation have to be confirmed and the cause investigated and corrected.

Confirmation of the accuracy of the calibration is performed at least every two months, with analyses of solutions of known concentrations from EMSL, EPA. The deviations of the results, compared to the real value, have to be less than 20%. For calculation of the accuracy, the following formula applies:

$$\% \text{ error} = \frac{\text{observed-known}}{\text{known}} \times 100$$

1.3.2 - Column Performance

New columns have to be tested for resolution with a p,p'-DDT solution. The computed efficiency has to be at least 2500 theoretical plates to be adequate.

Monitoring of decomposition or absorption components, due to column contamination, is accomplished by monitoring the response factors of Endrin, p,p'-DDT and Methoxychlor.

1.3.3 - Matrix Spike Analysis

To monitor the efficiency of sample preparation in every batch of ten samples, one standard spiked clean water sample is analyzed and the recoveries recorded. Problems related to the preparation technique are detected by comparing recovery trends to long term averages, taking into account the standard deviation.

1.3.4 - Detection Limits

Concentrations of a standard mix representing the reportable detection limits are injected routinely for validation of detectability.

1.3.5 - Monitoring of Retention Times

Retention times for all components are established by "in batch" standard runs. The times are entered into a computing integrator which matches the sample retention times (relative to the surrogate standard Mirex) with the windows of the relative retention times from the standard run for component identification.

1.3.6 - Surrogate Standard Monitoring

To monitor method performance for each individual extract, all our samples and quality control runs are spiked with Mirex as a surrogate standard. The Mirex recovery has been found to be representative of the chlorinated pesticides in the priority pollutant scan. If the recovery of Mirex falls outside the established quality control limits, either the:

Data are recalculated if an error can be established, or other appropriate measures are taken for correction before reanalyzing the sample.

1.3.7 - Reproducibility of Duplicates

If positive samples, or known spiked matrix analyses, are run in duplicate, the results R1 and R2 are assessed for reproducibility. The following formula is used for calculation of the deviation D:

$$\% D = \frac{R2-R1}{\left(\frac{R1+R2}{2}\right)} \times 100$$

1.3.8 - Method Blank Analysis

For every batch of twenty samples or less, one "blank" water sample spiked with the surrogate standard is carried through the entire analytical scheme, to verify that no interfering substances are introduced by the reagents or methodology.

2.0 - QUALITY CONTROL PROTOCOL AND QUALITY ASSURANCE FOR ANALYSIS OF VOLATILE PRIORITY POLLUTANT PESTICIDES BY GC/MS/DS

2.1 - Summary of Analytical Method

The procedure follows the protocol of the EPA Method 624 for analysis of purgeable priority pollutants in the Federal Register, Volume 44, No. 233 (December 3, 1979).

The components are "purged" with helium, trapped on a three-component trap and thermally desorbed onto a packed GC column, where they are separated. The gas chromatograph (GC) is coupled with a mass spectrometer (MS), which serves as the detector. The mass spectra and chromatographic retention times are used for identification and the areas in the reconstructed ion chromatograms provide the data for quantification.

2.2 - Method Validation (QC)

2.2.1 - Calibration of MS Response

Response curves are established for each component by analyses of at least three different concentrations. Because of fluctuating sensitivity of the ion source, which is due to the differences in tuning, the absolute response factors are subject to constant changes. Therefore, internal standard quantification is applied and response factors relative to the internal standard 1,4-dichlorobutane are calculated from standard runs. These RRFs are stored in a user library in the computer system. Since internal standard method is used, long-term averages of the RRFs are used for quantification rather than factors from "in batch" standard runs. Quality control calculations for precision of the entered RRFs are performed using the software of the

computer data system and data are rejected that fall outside the quality control limits. EMSL QC samples are used to verify the accuracy of the calibration.

2.2.2 - Recovery and Precision

Comparison of the areas for direct injections with the areas for the purged run indicate the recoveries of the components during the purge and trap procedure. Parameters for the purging and desorption are optimized to yield at least 60% for bromoform and higher recoveries for all other purgeable (non-polar) pollutants.

Since the reponse factors for the standards are calculated from purged standards, the fluctuations of the response factors are indicative of the changes of the component recoveries in the purge and trap concentration step. The precision of the factor calibration is therefore simulataneously the precision of the concentration procedure.

2.3 - Routine Monitoring of Method Performance (QA)

2.3.1 - Ion Abundance Calibration

Ion ratios for test substance decafluortriphenylphosphine (DFTPP) are checked each day for compliance with EPA criteria. If the spectra do not comply, adjustments of source voltages are made while observing peak ratios and shaped for test substance FC43. After each new tuning, the software then calibrates time/intensity data for FC43 against time/mass data in the memory. After the tuning, DFTPP is re-injected for verification that the correct mass ratios have been achieved.

Decafluorotriphenylphophine Key Ions and
Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30-80% of Mass 198
68	less than 2% of Mass 69
70	less than 2% of Mass 69
127	30-70% of Mass 198
197	less than 1% of Mass 198
198	base peak, 100% relative abundance
199	5-9% of Mass 198
275	10-30% of Mass 198
365	at least 1% of Mass 198
441	present, but less than Mass 443
442	greater than 40% of Mass 198
443	17-23% of Mass 442

2.3.2 - Detection Limits

Injections of standards of detection limit quantities are examined for peak sizes and positive identification, i.e., the ion abundance has to satisfy the "fit" threshold.

2.3.3 - Monitoring of Retention Times

The entries in the user library for the relative retention times of the components are updated with "in batch" standard runs. Relative retention times are computed relative to the internal standard 1,4-dichlorobutane.

2.3.4 - Matrix Spike Analysis

All standard runs for factor calibrations represent matrix spike analyses in the case of the volatile pollutants.

2.3.5 - Reproducibility of Duplicates

The data for duplicate samples or standards have to meet quality control limits for the deviation D, determmined from the two results R1 and R2:

$$\% D = \frac{R2-R1}{\left(\frac{R1+R2}{2}\right)} \times 100$$

2.3.6 - Method Blank Analysis (Instrument Blank)

In the purge and trap procedure, organic compounds "outgassing" from the plumbing account for the majority of contamination problems. Cross-contamination can occur whenever high level and low level samples are sequentially analyzed. To guard against cross-contamination, a blank -- organic free water -- is run after high samples to demonstrate that the system is free from contamination.

3.0 - QUALITY CONTROL PROTOCOL AND QUALITY ASSURANCE FOR SEMI-VOLATILE POLLUTANT ANALYSIS (PHENOLS AND BASE NEUATRALS) WITH GC/MS/DS

3.1 - Summary of Analytical Method

Our in-house analytical protocol corresponds to the EPA Method 625 for Analysis of Semi-Volatile Priority Pollutants, as published in the Federal Register, Volume 44, No. 233 (December 3, 1979).

Extraction of all components of interest is accomplished by extracting at acidic and basic pH. The concentrates of the two extracts are combined for analysis on a fused silica capillary column, which represents the optional version of EPA Method 625.

3.2 - Method Validation (QC)

3.2.1 - Calibration of Mass Spectrometer Response

The quantification by "internal standard" method is employed, that is, concentrations are computed with response factors relative to an internal standard (D10 Anthracene). These factors are entered from the files of standard runs into a "user library" in the computer. Response curves are first developed for various concentrations to establish ranges of linear response. The software permits application of selected RFs, averages or quadratic curve. For the priority pollutants, averages within the linear range are applied for quantification.

Calibration factors, relative to D10- Anthracene, are confirmed with "known" solutions from EMSL, EPA and the accuracy of quantification is established.

3.2.2 - Evaluation of Procedure for Recovery and Precision

Clean water spiked with standard solutions are carried through the analytical scheme to demonstrate ability to recover and analyze the components. Not enough data have been developed thus far for statistical evaluation of the precision of the recovery data.

3.3 - Routine Monitoring of Method Performance (QA)

3.3.1 - Ion Abundance Calibration of Mass Spectrometer

The electrical parameters of the ion source and quadropole are tuned and calibrated with the test substance FC43 until optimized to produce a satisfactory spectrum with an injection of decafluorotriphenylphosphine (DFTPP). Compliance with the EPA criteria for the ion abundance of DFTPP is documented on a daily basis.

3.3.2 - Performance of Fused Silica Capillary Column (FSCC)

For monitoring the capillary column performance, a special test mix ("Grobe" mix) is injected before a series of tests are undertaken. The response ratios of polar and non-polar components, as well as acid and basic compounds, have to remain within defined limits.

3.3.3 - Detection Limits

Detectability of the reportable concentration levels is verified by injections of low standards. This has to be repeated periodically, because of changing chromatographic column conditions and varying mass spectrometer sensitivity.

3.3.4 - Monitoring of Retention Times

The entries for the relative retention times of the components in the "user libraries" are updated by entering the files from routinely run "in batch" standard runs. Windows for the retention times are set in the libraries as criteria for automatic component identification.

3.3.5 - Stability of Response Factors

The response factors from the routine standard injections are added to the response factor file in the user library. Quality control evaluation of the factor lists permits detection of instrument malfunctions or errors related to "bad" solutions or calculation errors.

3.3.6 - Matrix Spike Analysis

Information gained from routinely performed analyses of standard spiked blank water is incorporated into the records for component recovery and is used for statistical evaluation of precision of the analytical method.

3.3.7 - Surrogate Standard Monitoring

Before extraction of samples, fluorinated and deuterated components are added to each sample to permit determination of the extraction efficiency from the recovery of these "surrogate" substances. The components that are used as surrogate standards to be extracted with the base neutral fraction are D_6-nitrobenzene and D_8-naphalene. Adequate phenol extraction is verified from the recoveries of the surrogate spikes of D_6-phenol and 2-fluorophenol.

3.3.8 - Reproducibility of Duplicates

No quality control limits have yet been set for acceptability of duplicate results. Guidelines are being developed from data of the analyses of standard spiked water.

3.3.9 - Method Blank Analysis

Interferences introduced during sample preparation are detected in "method blanks". Organic-free water, spiked with the surrogate standards only, are included in each batch of 20 samples or less.

4.0 - TRADITIONAL CHEMISTRY, INORGANICS AND HEAVY METALS

4.1 - Methodology

4.1.1 - Phenols

Phenolic materials react with 4-amino antipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable reddish-brown colored antipyrine dye. The intensity of color produced is a function of the amount of phenolic material present in the sample. Absorbance is measured at 460 nm. This method does not distinguish between the different types of phenols present, so pure phenol is used as the calibration standard and all phenols present in a sample are reported as phenol. This value will represent the minimum concentration of phenolic compounds in a sample.

The method recommends preserving samples at the time of collection with copper sulfate and acidifying with phosphoric acid to a pH of 4.0, refrigerating at 4°C, and analyzing within 24 hours. Recent studies ("Preservation of Phenolic Compounds in Wastewaters," Environmental Science and Technology, March 1978) indicate that if the above preservation procedure is followed, samples are stable up to 12 days. Preserving samples with sulfuric acid or sodium hydroxide and refrigerating at 4°C have been shown to maintain sample stability up to 28 days.

4.1.2 - Total Cyanides

Cyanides in the form of hydrocyanic acid are released from cyanide complexes by means of a reflux-distillation procedure, and absorbed in a sodium hydroxide solution scrubber. The cyanide ion in the scrubber solution is converted to cyanogen

chloride (CNCl) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to cyanate. Color is formed by the addition of a pyridine-barbituric acid reagent. Absorbance is measured at 578 nm.

4.1.3 - Metals

The following parameters will be analyzed by atomic absorption (or emission): calcium, magnesium, sodium, potassium, aluminum, iron, manganese, antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc. The instrumental operating conditions for these parameters are shown in Table 4-1.

4.1.3.1 - Sample Preparation, Except Mercury

Clean water samples require no special preparation. Samples are collected in bottles pre-acidified with nitric acid.

4.1.3.2 - Analysis

Iron, manganese, calcium, magnesium, aluminum, antimony, barium, beryllium, cadmium, chromium, copper, iron, nickel, silver, thallium and zinc are analyzed by flame atomic adsorption. Lanthanum is added to aliquots of sample prior to calcium and magnesium analyses to eliminate phosphorus interference. Sodium is added to aliquots of sample prior to barium analyses to reduce ionization interference. The instrument is calibrated with one to three standards to read directly in concentration. Three standards are re-analyzed to verify the linearity of the calibration range. Samples are then aspirated into the flame and the results are displayed directly in concentration units.

TABLE 4-1

TRACE METAL ANALYSIS CONDITIONS

Perkin-Elmer AA 5000

ELEMENT	WAVE LENGTH (nm)	BAND WIDTH (nm)	ATOMIZATION MODE	GRAPHITE FURNACE (°C/sec.) DRY	CHAR	ATOMIZE	CALIBRATION STANDARDS
Mercury	253.6	0.7L	Flameless Cold Vapor	-	-	-	2,3,4,5,6 ug/l
Thallium	276.8	0.7L	Flame, Air C_2H_2	-	-	-	0.2, 0.4, 1,2,4 mg/l
Beryllium	234.9	0.7H	Flame, N_2O-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Nickel	232.0	0.2H	Flame, Air-C_2H_2	-	-	-	0.2, 0.4, 1,2,4 mg/l
Iron	248.3	0.2H	Flame, Air-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Copper	324.7	0.7H	Flame, Air-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Zinc	213.9	0.7H	Flame, Air-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Silver	328.1	0.7H	Flame, Air-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Antimony	217.6	0.2H	Flame, Air-C_2H_2	-	-	-	1,5,10,20,50 mg/l
Cadmium	228.8	0.17H	Flame, Air-C_2H_2	-	-	-	0.2, 0.4, 1,2,4 mg/l
Chromium	357.9	0.7H	Flame, Air-C_2H_2	-	-	-	0.2, 0.4, 1,2,4 mg/l
Manganese	279.5	0.2H	Flame, Air-C_2H_2	-	-	-	0.3, 1,2,5,10 mg/l
Aluminum	309.3	0.7H	Flame, N_2O-C_2H_2	-	-	-	0.1, 1,2,5,10 mg/l
Calcium	422.7	2.0H	Flame, Air-C_2H_2	-	-	-	1,5,10,20,50 mg/l
Magnesium	285.2	0.7H	Flame, Air-C_2H_2	-	-	-	1,5,10,20,50 mg/l
Sodium*	589.2	0.14H	Flame, Air-C_2H_2	-	-	-	1,5,10,20,50 mg/l
Potassium*	766.9	4.0H	Flame, Air-C_2H_2	-	-	-	1,5,10,20,50 mg/l
Lead	283.3	0.7L	Graphite Furnace	125/30	500/30	2700/12	2,5,10,20,50 ug/l
Arsenic	193.7	0.7L	Graphite Furnace	125/30	1200/30	2700/12	2,5,10,20,50 ug/l
Selenium	196.0	2.0L	Graphite Furnace	125/30	1200/30	2500/5	2,5,10,20,50 ug/l

*Instrument run in emission mode.

Arsenic, lead and selenium analyses are performed by graphite furnace atomic absorption. For each element, five to seven standards are prepared. For each of these elements, an additional solution is added to both samples and standards (e.g., lanthanum nitrate is used to suppress sulfate interference in the lead analysis, hydrogen perioxide and nickel nitrate are used in arsenic and selenium to keep ions in the appropriate valence state and prevent premature volatilization of the analyte). Aliquots of standards and samples are added to small cups and placed in a tray of the Perkin-Elmer AS-1 auto-sampler. The auto-sampler is set to inject 20 ul of standard of sample into the graphite furnace. The instrument automatically proceeds through programmed drying, charring and atomization cycles. A signal proportional to the amount of element present is produced during the atomization cycle and is recorded as a peak height on the chart recorder. A numeric value for the peak is also recorded on a printer.

A calibration curve of peak height versus concentration is constructed from the blank and standards data. Quantification is accomplished by subtracting the blank value from peak heights of samples and reading the concentration values from the constructed calibration curve. If necessary, due to matrix interferences in the samples, the samples can be quantified using the method of standard additions. Deuterium arc background correction is used to minimize background scattering interference.

The graph of standard additions plot should be linear, and the slope of the sample results should be within 20 percent of

the slope of the pure standards for the standard method additions to be reliable. If the above criteria are not met initially, dilution of the sample will usually enable the standard additional method to produce acceptable data.

4.1.3.3 - Mercury (Preparation and Analysis)

Analysis for mercury requires a separate digestion procedure (245.1.8.1, "Methods for Chemical Analysis of Water and Wastes"). Digestion is accomplished by placing 50 ml of sample in a 300 ml BOD bottle and adding 2.5 ml sulfuric acid, 1.25 ml nitric acid, and 7.5 ml 5% potassium permanganate solution. Additional portions of potassium permanganate solution are added until the purple color persists. Potassium persulfact (8 ml) is then added and the samples are heated in a water bath at 95°C for two hours. After cooling, 6 ml of a sodium, chlorid-hydroxyamine sulfate solution is added to reduce excess permanganate.

Analysis is completed on a Perkin-Elmer AA 5000 atomic absorption spectrophotometer, in conjunction with a Perkin-Elmer MHS mercury-hydride generator. An open end tubular cell is placed in the light beam from a mercury electrodeless discharge lamp. The cell is connected with tubing to the MHS-10. A 10 ml aliquot of digested sample is placed in a reaction vessel which is then attached to the MHS-10. A solution of sodium borohydride is then pumped into the reaction vessel. Mercuric ion is reduced to free mercury which is swept from the reaction vessel into the cell with argon gas. The resulting absorption of light at 253.6 cm is proportional to the amount of mercury being swept through the cell.

Standard solutions of mercury are digested and analyzed with the samples. The data generated by the standard solutions are used to prepare a calibration curve. Sample data are calculated from the calibration curve.

4.2 - Quality Control

Analytical quality control is maintained by monitoring precision and accuracy. Data use in determining precision are obtained by analyzing 15% of all samples in duplicate. Percent recovery data are used to monitor accuracy.

These data are obtained by analyzing a replicate of a sample to which a known amount of analyte has been added (a spike). For BOD, COD and TOC, special surrogate samples of glucose and glutamic acid are prepared and analyzed.

Accuracy is also monitored and controlled by analyzing samples of known value prepared by an independent source (EPA EMSL Laboratory).

4.2.1 - Precision (R-bar charts)

For each parameter tested, R-bar charts are prepared according to the procedures detailed in EPA's Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA 1600/4-79-019).

Fifteen percent of all samples are analyzed in duplicate. The absolute value of the difference between the results of two duplicates is plotted on the R-bar chart. Values falling below the control limits require corrective action.

4.2.2 - Accuracy (X-bar charts)

Fifteen percent of all samples are analyzed for percent recovery. In general, the amount of spike added to a sample is approximately equal to the amount of analyte in the sample. The percent recovery is calculated using the following formula:

$$\% \text{ recovery} = \frac{Ss - So}{S} \times 100$$

where: So is the amount of analyte in mg/l in the original sample
Ss is the result in mg/l from the analysis of the spiked sample
S is the amount of analyte in mg/l spiked into the original sample

The percent recovery is then plotted on an X-bar chart which has been prepared according to the details in the EPA QC Handbook. Values of percent recovery falling within the control limits are acceptable. Values of percent recovery falling outside the control limits require corrective action.

4.2.3 - Corrective Action

4.2.3.1 - QC Data Values Between Warning Limit and Control Limit

When QC data value falls between a warning limit and a control limit, the sample is re-analyzed. If the second value is acceptable, analysis of other samples is continued. If the second value is again between the warning limit and control limit, analysis is halted, and all aspects of the analytical process are examined, including reagents, standards and instrumental operating conditions. Any suspect conditions are corrected. The sample which generated original unacceptable QC data value is

again re-analyzed. QC data value is obtained and analysis is continued. If an unacceptable value is obtained, the check-out process is repeated.

4.2.3.2 - QC Data Values Outside Control Limits

The procedure is the same as in 4.2.3.1, except that all samples analyzed since the last "in-control" QC data point are re-analyzed.

UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON 98195

School of Public Health and Community Medicine
Department of Environmental Health, SC-34

Tom Brisbin
PRC Consoer Townsend
Chicago, Illinois

Dear Mr. Brisbin:

In response to your inquiry of this date, the samples analyzed for priority pollutants for you in 1981 were run under a quality control program that we originated prior to the EPA program now in effect. We were reponsible for one of the two major EPA grants to develop analytical methods for priority pollutants from 1978 to 1980, and the quality control program we devised is basically the one used for your samples.

Although EPA has since elaborated the analysis considerably, the program we used contains many of the same elements: use of surrogate or stable-isotope standards to determine recovery, frequent recalibration of instrument response, blank and spiked analyses, etc. The enclosed exerpt from our final report on the EPA project describes the program as we originally devised it. This description will differ from the procedures that we followed for your samples only in details.

I hope that this response is sufficient; please don't hesitate to contact me for further elaboration if necessary.

Sincerely,

D. Kalman
Director
Trace Organics Analysis Center

SECTION 9

PROPOSED QA/QC PROGRAM FOR POTW SAMPLES

The elements of this proposal are derived from the following key EPA documents: a November 1978 results summary of the Cincinnati POTW sources pilot study QA/QC program (conducted by Arthur D. Little, Inc.); an Arthur D. Little Company handout prepared for an EPA contractors' meeting on method development March 9, 1979; "Recommended Sediment and Sludge Sample Collection Procedures for Priority Pollutant Analysis, addendum to Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Compounds (March 1979, EPA - Cincinnati ENSL documents); and BAT Screening Protocols.

QA/QC consists of the following elements: contamination control, containment/recovery of sample, and instrumental calibration. For each element, one phase of the QA/QC program is needed. Contamination control is addressed by carefully defining materials and cleaning procedures for all sampling and preparation materials, and is monitored by blank determinations. Field blanks consist of distilled, organic free water samples exposed to the same glassware and manipulations as a real sample. Lab blanks consist of an aqueous blank run through the extraction/cleanup steps. Containment/recovery is also dependent on sampling and handling technique and is monitored by recovery standards spiked into actual or blank samples. The recovery standards may be model compounds ("surrogates") or mixtures of the actual priority compounds. Instrumental calibration is ensured by the use of external standards to tune instruments uniformly and internal standards to provide cross checks---detecting losses during injection or in procedures occurring between addition of separate standards, as well as monitoring the integrity of each internal standard.

Figure 9-1 shows a schematic representation of the use of various types of standards to monitor QA/QC for different segments of the analysis. The inclusion of specific, noninterfering compounds to provide QA/QC information requires only minimal effort for GC/MS analysis, and is therefore a preferable alternative to parallel analyses of samples unspiked and spiked with priority pollutants.

The actual structure of a QA/QC program has two logical phases -- initiation and maintenance. In the initiation phase, the analysis method is verified by repeated determinations and is shown to be statistically reliable. Laboratories just beginning to follow EPA methods, or applying alternative procedures not yet in routine use, will determine what, if any, experimental problems exist during the initiation phase.

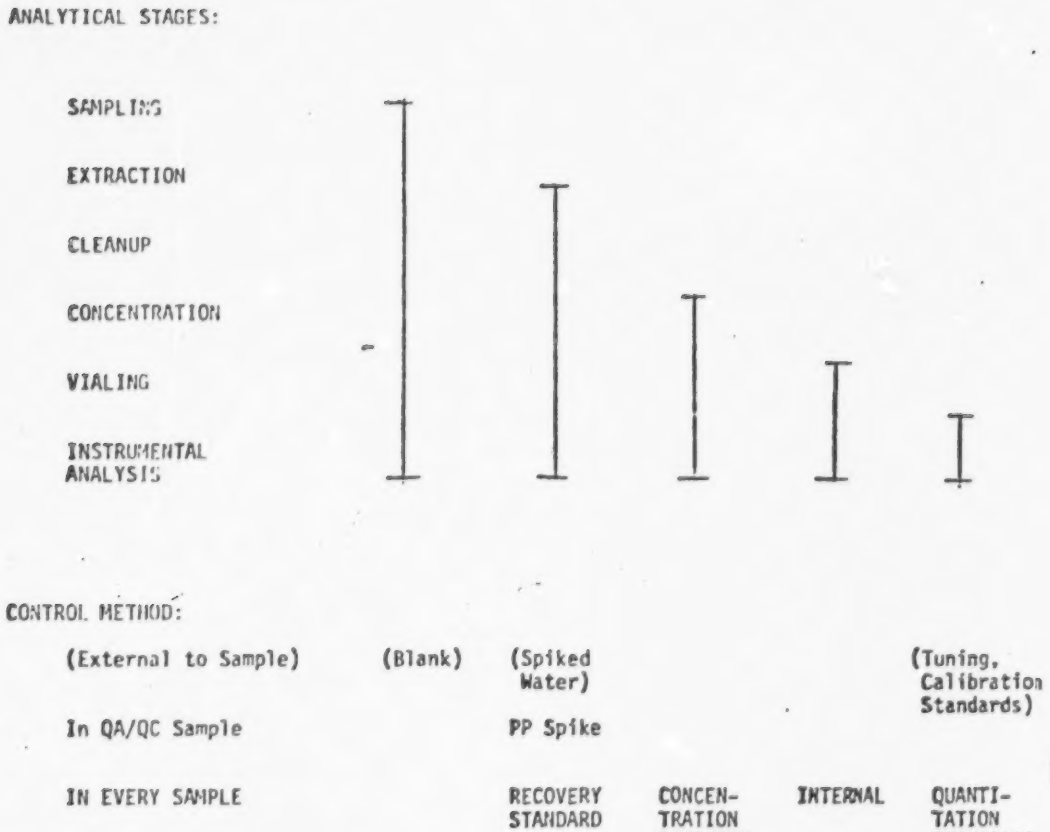

Figure 9-1 Use of Standards and Spiked Compounds

EPA has suggested a 12-fold initiation program involving six sets of replicate determinations of surrogate spiked and priority pollutant spiked samples, with three concentration levels of the spikes. This program provides enough repetition for statistical validation, but is inconvenient in that it does not permit many real analyses to take place concurrently. A reasonable modification would be to perform the different spike concentration replicates on different (but preferably similar) samples. This would permit three real analyses rather than one. The necessity of determining recoveries at three concentration levels, rather than two, is also debatable. It is the extremely low concentration range where QA/QC is most important, and most difficult. Determinations at 1 ppb and 100 ppb might be acceptable in lieu of the prescribed 2x, 10x, and 100x spikes.

Maintenance of QA/QC involves specific analyses to "measure" known spike concentrations. The EPA proposal for a routine QA/QC maintenance sample is: 1) the unspiked sample, 2) a spiked sample, 3) a replicate spiked sample, 4) a spiked distilled water sample, and 5) a system blank. If one sample in 10 is a QA/QC sample, then 14 analyses will be required to produce 10 sets of real data (40%). The following modification is proposed: each sampling event needs a field blank and, if 5 samples are taken on one day or at one time or with one set of glassware or reagents, a blank should accompany this set. The need for replicate analyses to demonstrate reproducibility could be met with suitable recovery compounds in the (sample and sample + spike) pair of analyses. The choice of what type of sample to use for QA/QC (influent, sludge, etc.) will significantly effect the final recoveries seen, since background varies substantially among sample types. Therefore, the importance in appropriate model compounds to provide recovery QA/QC information on each sample cannot be over-emphasized. At present, the choices of available surrogates is limited. Table 9-1 presents the EPA recommendations, as well as those in use at the University of Washington. A satisfactory set of model compounds should represent the range of chemical and physical behavior of the priority pollutants, and may need to contain specific models for difficult (reactive) compounds as well. Perfluorinated compounds have substantially different physical properties from their perproteo counterparts but, together with a limited number of deuterated and C-13 labelled priority compounds, presently are all that is available. Specific classes of priority compounds, such as phthalates and halogenated ethers, have no model currently available. As better sets of model compounds not present in the environment are developed, appropriate reductions in the number of spiked samples could be achieved, with an increase in QA/QC.

One example of the use of multiple compounds for recovery and quantitation is the volatile recovery standard currently in use. This standard consists of nine stable isotope-substituted priority compounds: chloroethane-d5; 2,2-dichloropropane-d6;

PURPOSE: COMPOUND	MS Tuning	GC Perform.	Internal Quan.Std VOA	Internal Quan.Std Extract	Recovery Standard VOA	Recovery Standard Extract	Concent. Recovery Standard	Reference Internal Standard
COMPOUND: (EPA)	$F_{10}B_3P$; F_5BrB (VOA)	Benzidine + Aldrin	$BrClCH_2$	D_{10}-Anthracene	none	Acids: F_5BOH o-FBOH Neutrals: F_{10}-biphenyl o-Fluoro-Aniline	none	none
COMPOUND: (U of W)	$F_{10}B_3P$; F_5BrB	Priority Pollutants	D_6Cl_2-propane D_8toluene Bromoform-D_1	D_8Naphthalene D_{10}Phenanthrene D_{12}Perylene	D_5Chloroethane D_1Chloroform D_6Benzene D_3Acetonitrile D_4Dichlorobenzene	EPA COMPOUNDS+ others as obtained	D_4Dichlorobenzene	Hexamethylbenzene

Table 9-1 Standard Compounds for QA/QC

chloroform-d; benzene-d6; toluene-d8; acrylonitrile d3; bromoform-d; and dichlorobenzene-d4. (The underlined compounds are GC quantitation standards; the rest are included for recovery data and to cross check the quantitation standards).

In the sampling phase for the current project R806102-01, the proposed QA/QC program consists of: a) one field blank per sampling occasion (per plant sampled), b) one QA/QC sample per two plants (approximately 1 in 10 samples), c) recovery compounds to be used in every sample, d) use of recovery compounds to provide replicate verification rather than a second spiked sample (the second spiked sample will be taken and extracted, and the extracts archived), e) an expanded set of standards/recovery standards for VOA as shown in Table 9-1, f) one blank per each VOA analysis, g) replicate VOA analyses for those samples indicated by poor recovery of spiked standards, and h) expansion of recovery standard list and eventual reduction of frequency of spiking to 1 in 20 samples.